

Nitrogen-doped graphene-like carbon material derived via a simple, cost-effective method as an excellent adsorbent for methylene blue adsorption

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Abstract. Nitrogen-enriched graphene-like carbon materials were successfully prepared via pyrolysis of a mixture of melamine, ammonia chloride (NH₄Cl) and polyvinyl pyrrolidone (PVP) at a mild temperature without inert gas protection. Different techniques were used to analyze the physical and chemical properties of the products. All the prepared materials showed excellent performance in methylene blue (MB) adsorption. In particular, the materials prepared with 3 g polyvinyl pyrrolidone (PVP) (NCG-2) exhibited the best performance, a very high maximum adsorption capacity of 348.2 mg/g, much larger than many reported materials. The high adsorption capacity of the Nitrogen-doped graphene-like carbon materials was possible due to its uniform porous structure, high specific surface area. Moreover, NCG-2 could be recycled and only a only slightly decreased in the removal efficiency were observed after 5 cycles.

1 Introduction

Recently, water pollution arisen from dyes has attracted much attention.[1] Hence, it is critical to remove dye from wastewater. Various methods have been developed, such as photo-catalytic de-composition[2] and chemical oxidation-reduction[3-4]. However, high energy consumption and operational costs severely hindered these methods for dye treatment in large-scale application. Alternatively, adsorption has already been applied for dye treatment applications due to its low-cost and easily adaptable property.[5-7] In recent years, many dye adsorbents have been explored, such as chitosan[8] and zeolite[9]. Among all such adsorbents, carbon-based materials have received more attention due to their high efficiency for dye adsorption and the prevention of secondary pollutants.[10-13] To further enhance the dye adsorption capacity of carbon materials, preparing carbon materials with large surface area, appropriate pore size or modified surface properties are the main methods used to obtain better dye performance. Heteroatom doping is often deemed an effective way to obtain the abovementioned features of carbon-based materials. In particular, nitrogen (N) has been broadly studied as one of the most attractive and widely used heteroatom dopants. Studies have demonstrated that N doping could enhance the interactions by modifying the surface charge properties via electrostatic attraction.[14-15] According to recent studies, nitrogen-doped carbon can significantly increase dye adsorption ability, especially for anionic dyes.[16-17] However, the doping concentration is usually low (less than 7%), which leads

to inefficient adsorption performance.[18-19] Furthermore, doping typically requires additional processes to add heteroatom-containing chemicals as dopant sources into pre-synthesized carbon materials, which render the resulting materials less competitive than other adsorbents.[20-21] Thus, a facile method to achieve the post-synthesis high-concentration N doping of carbon-based adsorbents remains highly desired yet challenging.

Herein, we report a simple and cost-effective approach to fabricate nitrogen-enriched graphene-like carbon materials by pyrolysis of a mixture of melamine, ammonia chloride (NH₄Cl) and polyvinyl pyrrolidone (PVP) at a mild temperature (600°C) without inert gas protection. The obtained N-doped carbon demonstrated a graphene-like interconnected nanosheet network, a high N content of over 15% and a high specific surface area of 432 m²/g. When the products were used as adsorbent to adsorb the methylene blue which was known as typical dye pollutant, the carbon material exhibits excellent adsorption performance and recyclability

2 Experimental

2.1 Synthesis of N-doped carbon materials

Typically, Melamine (3 g), NH₄Cl (3 g) were mixed via directly grinding together in the presence of different amounts of polyvinyl pyrrolidone (PVP) (0 g, 1.5 g, 3 g and 4.5 g) and calcinated at 600°C for 240 min with a suitable heating rate (5°C/min). Finally the black powder

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obtained. The products were denoted as NCG-0, NCG-1, NCG-2 and NCG-3, respectively. For comparison, the samples prepared via the mixture in the absence of the NH_4Cl (3 g melamine and 3 g PVP) was also conducted under similar conditions, named as NCG-2-N.

2.2 Characterization

The structures of the products were analyzed by X-ray diffraction (XRD). Morphologies of the carbon materials were observed by the Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The ASAP2420 surface area analyzer was utilized to study the specific surface area and pore texture of the products.

2.3 Adsorption experiments

In experiment, the 40 mL solution which contained 10 mg adsorbents (NCG-2-N, NCG-1, NCG-2 and NCG-3) with different MB concentration (80 mg L^{-1} - 120 mg L^{-1}) at different pH (3-11), temperatures (298.15 K - 318.15 K) were conducted. The UV-vis spectrophotometer were used to determine the MB concentration (wave length= 665 nm). After adsorption, the adsorbent (NCG-2) was suspended with solution which contained suitable concentration of HCl and HNO_3 accompany with shaken over-night, then collected, washed and dried for 12 h. The adsorption amount (mg g^{-1}) was calculated via Eq. (1):

$$Q_t = (C_0 - C_t)V/W \quad (1)$$

Where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the initial and remaining MB concentration after adsorption for t (min), respectively. The volume (L) of the MB solution is represented by V used in experiment and w stand for the amount of the adsorbent used in the test (g).

3. Results and discussion

3.1 Material characterization

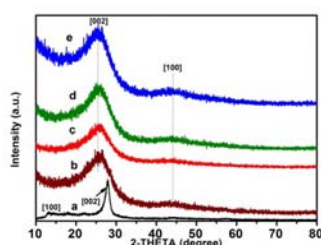


Fig. 1 The XRD pattern of the prepared products: a) NCG-0; b) NCG-N-2; c) NCG-1; d) NCG-2 and e) NCG-3.

As shown in Fig. 1 b-e, the products which prepared via PVP (Black powders) demonstrated two broad and low peaks at 26° and 43° could be obtained which demonstrated the products were formed by the carbon components. While the NCG-0 (Yellow powder) exhibited a significantly different pattern: two obvious

peaks located at 13.10° and 27.70° , which could be index to graphitic carbon nitride ($\text{g-C}_3\text{N}_4$). Therefore, PVP was a crucial component for obtaining N-doped carbon materials.

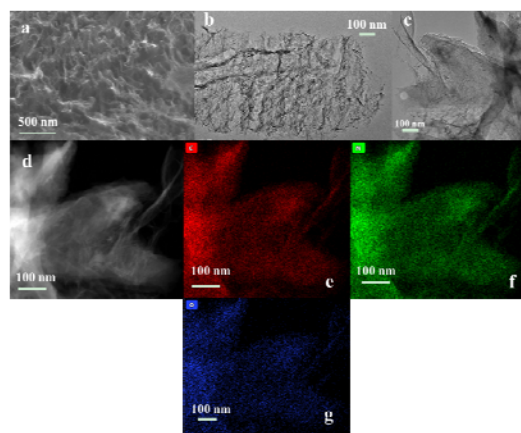


Fig. 2 (a) SEM, (b,c) TEM images, (d) EDS mapping-STEM HAADF, (e-g) the corresponding EDS mapping for C (red), N (green), O (blue) of NCG-2.

The Fig. 2 exhibited the morphology and structure of NCG-2. According to the results of Fig. 3a-c, the product demonstrated a crumpled sheet layer-structure with a rough surface and uniform porous structure. The possible explanation would be that $\text{g-C}_3\text{N}_4$ with a layered structure could be formed at 500 - 600°C in the thermal treatment process.[22] At the same time, the aromatic carbon in the PVP could adhere to the $\text{g-C}_3\text{N}_4$ template, thus forming a layered $\text{g-C}_3\text{N}_4/\text{PVP}$ structure.[23] Then the $\text{g-C}_3\text{N}_4$ began to carbonize and exfoliate in the presence of PVP, then shrank to form layer structures, meanwhile the gas release by PVP and NH_4Cl favored the porous formation. The elemental mapping with energy-dispersive X-ray spectroscopy (EDS) graph were used to analyze the elemental composition of the NCG-2. The scanning transmission electron microscopy high-angle annular dark-field imaging (STEM-HAADF) image (Fig. 2d) and the corresponding elemental mapping (Fig. 2 e-g) showed that the NCG-2 were composited by C, N and O, which demonstrated that the successful preparation of the Nitrogen-doped carbon material. Interestingly, according to Fig. 1s, the amount of PVP added influences the material morphology to some extent. For the NCG-1 sample (Fig. 3 d-f), obvious agglomerated chunks can be observed in the crumpled sheet structures. While NCG-3 (Fig. 3 g-i) demonstrated a dual-porosity structure with less porous. The insufficient PVP addition were not favor for the interaction with the $\text{g-C}_3\text{N}_4$, while more PVP adding, the structure of the PVP polymer chain is transformed from linear to quasi-circular, which were not benefit for the porous formation. Therefore, suitable amount of PVP would be crucial to obtain the porous layer-structure materials

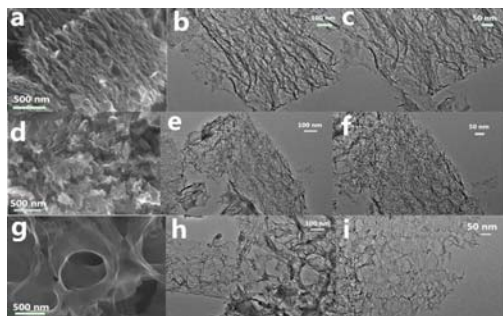


Fig. 3 (a) SEM, (b-c)SEM image for NCG-2-N; (d) SEM, (e-f)TEM image for NCG-1; (g) SEM, (h-i)TEM image for NCG-3

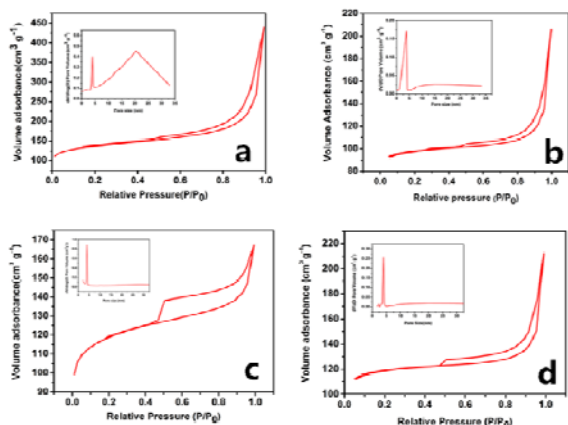


Fig. 4 N₂ adsorption/desorption isotherms and pore size distribution (inset) of a) NCG-2; b) NCG-2-N; c) NCG-1 and d) NCG-3;

The N₂ adsorption-desorption isotherms were demonstrated an effective way to analyze the specific surface area and structure porosity. According to the Fig. 2, all the carbon-based materials yield a type II isotherm. The BET surface area of NCG-2 was calculated as 432 m² g⁻¹, which is the much larger than the other samples and the pore size of NCG-2 were distributed at 4 nm (mesopores) and 25 nm (large mesopores). In addition, the BET surface areas of NCG-2-N, NCG-1 and NCG-3 were 299, 364 and 370 m²/g, respectively (shown in Table 1). Moreover, the pore volume of NCG-2 was 0.681 cm³ g⁻¹, which was great higher than the other products. The high BET surface areas could provide more space for MB molecules to active sites of the adsorbents, and the large pore volumes enhanced the possibility unimpeded transference of the MB in the adsorbents.

Table 1 Textural Properties of the products

| Samples | BET surface areas (m ² /g) | Pore Volume (cm ³) |
|---------|---------------------------------------|--------------------------------|
| NCG-2-N | 299 | 0.199 |
| NCG-1 | 364 | 0.234 |
| NCG-2 | 432 | 0.681 |
| NCG-3 | 370 | 0.259 |

3.2 MB adsorption

To test the MB adsorption performance of the nitrogen-enriched graphene-like carbon materials, in this work, NCG-2-N, NCG-1, NCG-2, and NCG-3 were selected as the adsorbents. The MB adsorption performance was studied as a function of adsorption time (t). According to Fig. 4, within the first 15 min, the adsorption capacity of NCG-2 for MB could reached 165 mg g⁻¹, while only lower than 100 mg g⁻¹ in other samples were obtained. The NCG-2 exhibited excellent adsorption performance, and the capacity was approximately 347.1 mg g⁻¹ when attaining the equilibrium. The corresponding values for NCG-2-N, NCG-1 and NCG-3 were 134.1 mg g⁻¹, 223.1 mg g⁻¹ and 181.5 mg g⁻¹, respectively, which were lower than those of NCG-2. According to the analysis above, it is believed that high specific area and the N dopant were respond for the excellent performance of NCG-2 as a dye adsorbent. In addition, the uniform porous structure of NCG-2 could also improve the affinity for MB molecules.

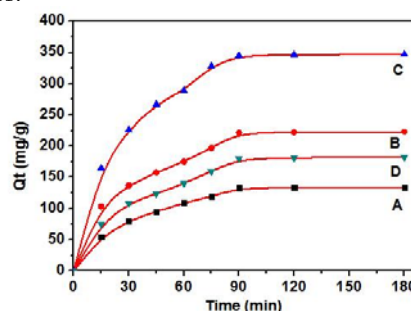


Fig. 5 MB adsorption kinetics curves for carbon-based materials: (A) NCG-2-N; (B) NCG-1; (C) NCG-2; and D) NCG-3.(100 mg/L MB, pH=7, reaction temperature=298.15 k)

3.3 Regeneration of NCG-2

As an important adsorbent evaluation index, the recycling utility of NCG-2 was also determined. After the adsorption test, the NCG-2 was collected, washed several times, and then dried overnight. The process was repeated 5 times to evaluate NCG-2 reusability. In Fig. 9, the adsorption capacity of NCG-2 drop slowly (from 347.1 to 328.8 mg g⁻¹) after five cycles, which demonstrated the good stability and reusability of NCG-2 as an adsorbent in MB treatment.

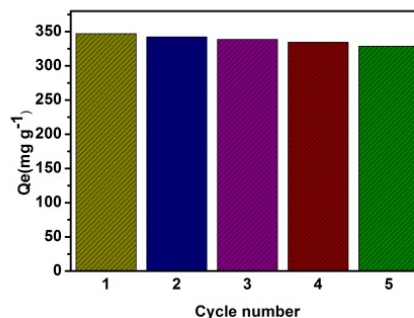


Fig. 6 The reusability of NCG-2 for MB

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