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Research article

# Nitrogen-enriched carbon sheet for Methyl blue dye adsorption

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ABSTRACT

In this work, nitrogen-enriched carbon sheet (NECS) was successfully fabricated by using sodium gluconate as a carbon source via melamine assisted chemical blowing approach. The obtained material exhibits sheet-like morphology with ultra-thin thickness and has a high specific surface area of 604 $m^2g^{-1}$ and high nitrogen contents of 11.2 wt%. The NECS showed an excellent adsorption performance towards the removal of anionic dye Methyl blue (a-Mb). The adsorption of a-Mb onto NECS better fitted the Langmuir isotherm model with the highest adsorption capacity of 847 mg $g^{-1}$. Interestingly, the NECS showed a pH-sensitive behavior towards the adsorption efficiency of a-Mb dye in which the adsorption capacity abruptly increased from 34 to 701 mg $g^{-1}$ when the pH of the solution was decreased from 10 to 2. Furthermore, the adsorbed materials can be easily regenerated without obvious efficiency loss over a five adsorption-desorption cycles.



## 1. Introduction

Water pollution from a variety of dyestuff industries has become an alarming serious environmental issue (Yang et al., 2015). These water posses some sort of colors which are tedious to treat because of their aromatic structures and non-biodegradable nature (Mittal et al., 2007). The presence of these dyes greatly affect the water quality as such dyes are aesthetically unpleasant, carcinogenic, retard light penetration thus, can affect aquatic life and food chain (Chen et al., 2010). Therefore, it is imperative to treat the dye bearing water before discharge.

To date, several approaches have been identified for the removal of dyes including coagulation, solvent extraction, photocatalytic degradation membrane filtration, adsorption, chemical oxidation, and biological oxidation (Zhu et al., 2007; Labanda et al., 2011; Liang et al., 2014; Manenti et al., 2014; Lin et al., 2015; Xu et al., 2015; Zhao et al., 2015). Among them, adsorption is the most facile, cheap and efficient approach, because of their high elimination performance, simple and easy operation procedure and rife availability of different adsorbent materials (Zhao et al., 2011). Thus, substantial research concern has been exerted by researchers all over the world to seek for novel adsorbents with high efficiency and large adsorption capacity.

Adsorption performance of organic dyes is essentially influenced by the porous morphology and functional groups of the adsorbent. Carbon-based materials owing to their enhanced efficiencies in water remediation and prevention of secondary pollutants have achieved more attention (Pereira et al., 2003; Dong et al., 2011; Smith and Rodrigues, 2015). In the endeavor to maximize the adsorption performance of carbon materials, much research has been focused on the fabrication of new materials with outstanding properties like high surface area, reasonable pore size, and suitable surface properties. Chemical doping with foreign atoms is an effective method to achieve the above-mentioned features of carbon-based material. A number of dopants have been introduced into the carbon matrix such as boron, phosphorous, sulfur, and nitrogen etc. Among the different available options, nitrogen doping of carbon materials have broadly studied. The corresponding research reports have demonstrated that nitrogen doping has a remarkable influence on the surface properties such as surface polarity; surface basic sites, electrical conductivity and electron donor. In the case of adsorption, nitrogen doping is beneficial to improve the hydrophilicity so that enhance the dispersion of adsorbents in the aqueous media. Moreover, the available surface with charged surface property induced by nitrogen doping can maximize electrostatic interactions between sorbent and adsorbate, thus enhancing sorption capacity (Czerw et al., 2001; Li et al., 2008; Ding et al., 2011; Schiros et al., 2012; Wood et al., 2014). Recently several works have reported that nitrogen-doped carbon has exhibited enhanced

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ability towards the sequestration of dyes especially anionic dyes (He and Hu, 2011; Liu et al., 2014; Sánchez-Sánchez et al., 2015). Hu and coworkers have reported the enhanced adsorption performance of anionic dyes including methyl orange by CMK-3 ammonia tailored mesoporous carbon compared with the microporous active carbon material (He and Hu, 2011). The enhanced adsorption performance was attributed to the electron donating effect of the introduced nitrogen-containing functional groups of the materials. However, the previously reported nitrogen-containing adsorbents are not much efficient due to low nitrogen contents and complexly operating procedures which render them less competitive. Thus, the novel carbon-based adsorbents with high removal performance are still highly desired, yet challengeable.

Contemporary nano-adsorbents with two-dimensional morphology has achieved great research concern owing to their versatile features such as huge specific surface area, the unique morphology, diffusion of ions and good mechanical stability. Usually, they are synthesized by strategies such as solvothermal, chemical vapor deposition, templating and mechanical exfoliation process (Wang et al., 2016). However, these approaches are monotonous, costly and utilize reagents that are highly toxic to the environment. Despite tremendous efforts to prepare nitrogen-enriched carbon sheet materials, to date, a method for facile, economic, and eco-friendly production still remains a stumbling block.

Herein, we report a straightforward approach to fabricate nitrogen-enriched carbon sheet (NECS) via chemical blowing approach using sodium gluconate as a carbon precursor and melamine as nitrogen and a blowing agent. As shown in Fig. 1 the synthesis protocol of the NECS is very simple involving the carbonization of sodium gluconate and melamine under nitrogen protection. Sodium gluconate is the sodium salt of gluconic acid derived from glucose fermentation which is nontoxic, cheap and easily biodegradable. These resultant NECS possesses a number of unique features which are required for an ideal adsorbent materials i.e. the sheet-like morphology, the high surface area and abundant functional groups. All these merits make NECS as the suitable adsorbent for the removal of a-Mb dye.

## 2. Experimental section

### 2.1. Chemicals

Sodium gluconate, Melamine, NaOH and HCl of analytical grade were purchased from Sinopharm Chemical Reagent (Beijing China) and used without any extra purification.

### 2.2. Materials synthesis

The nitrogen-enriched carbon sheet (NECS) was synthesized through a facile melamine assisted chemical blowing process utilizing sodium gluconate as a carbon precursor and melamine as nitrogen and a blowing agent. In general sodium gluconate and melamine were mixed with a mass ratio of 1:1 directly by grinding together and carbonized in a tube furnace at 850 °C at a rate of 3 °C $min^{-1}$. After carbonization, the obtained solid residue was washed with HCl (15%) to eliminate the sodium compounds. Finally, the NECS were collected by centrifugation and washed repeatedly with profuse de-ionized water till the pH of the supernatant solution was reached neutral and were dried at 105 °C for 24 h. For comparison sodium gluconate only denoted as (NaG) was also carbonized following the same procedure without melamine.

### 2.3. Characterization

FT-IR spectra were achieved using the KBr pellets technique on an FT-IR spectrometer (American Nicolet Corp. Model 170-SX) in a transmission mode. Nitrogen adsorption-desorption isotherms were collected at 77 K using a Micromeritics 2020 analyzer (USA). TEM (transmission electron microscopy) analysis was conducted on a TECNAI G2 20 LaB6 electron microscope operated at 200 kV. SEM (scanning electron microscopy) analysis was conducted on an FEI Quanta 250 F system. XRD patterns were recorded on a Bruker AXS D8 advance powder diffraction system using Cu K (= 1.5418 Å) radiation. The XPS spectra were obtained by using a PHI Quantera II ESCA System with Al Kα radiation at 1486.8 V. The residual amount of a-Mb dye was determined by PerkinElmer UV-Spectrophotometer.

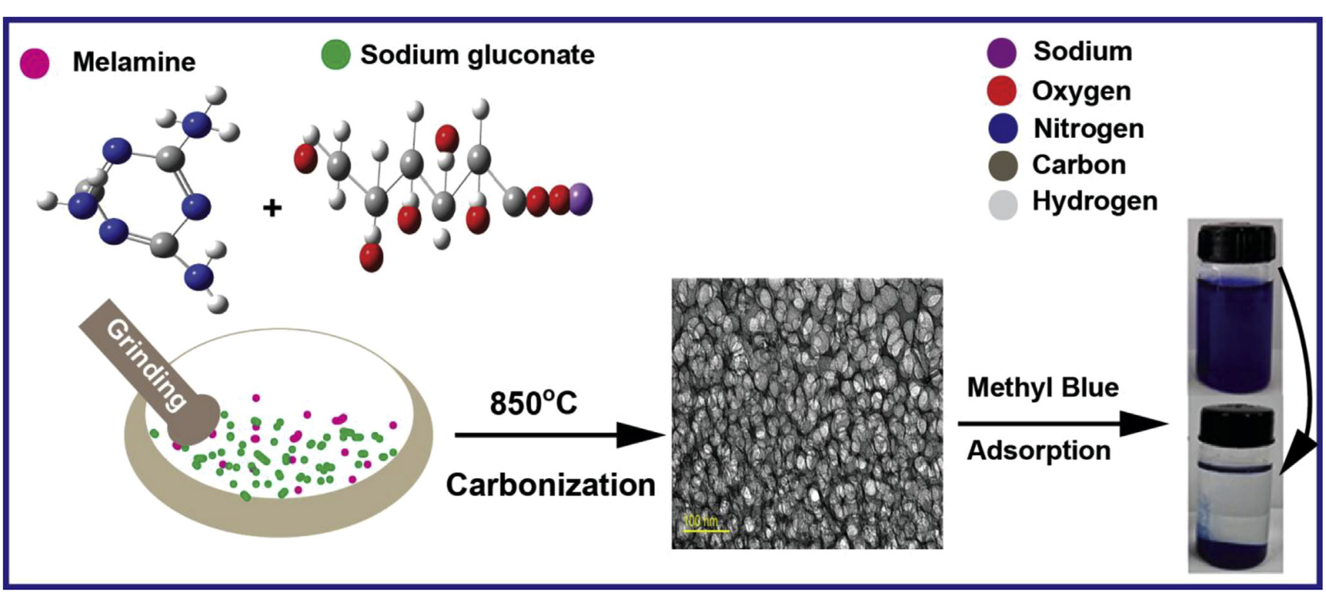


**Fig. 1.** Schematic illustration of the fabrication process of NECS and dye removal.