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Acid/base bifunctional carbonaceous nanomaterial with large surface area: Preparation, characterization, and adsorption properties for cationic and anionic compounds

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HIGHLIGHTS

- A simple and green method was proposed to prepare carbon nanomaterials.
- The carbon product showed acid/base bifunctional surface with large surface area.
- The carbon material could efficiently adsorb both cationic and anionic compounds.

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ABSTRACT

Nanostructured carbonaceous materials are extremely important in the nano field, yet developing simple, mild, and "green" methods that can make such materials possess large surface area and rich functional groups on their surfaces still remains a considerable challenge. Herein, a one-pot and environment-friendly method, i.e., thermal treatment (180 °C; 18 h) of water mixed with glucose and chitosan (CTS), has been proposed. The resultant carbonaceous nanomaterials were characterized by field emitting scanning electron microscope, N_2 adsorption/desorption, Fourier transform infrared spectroscope, X-ray photoelectron spectroscopy, and zeta-potential analysis. It was found that, in contrast to the conventional hydrothermally carbonized product from pure glucose, with low surface area (9.3 $m^2\ g^{-1}$) and pore volume (0.016 $cm^3\ g^{-1}$), the CTS-added carbonaceous products showed satisfactory textural parameters (surface area and pore volume up to 254 $m^2\ g^{-1}$ and 0.701 $cm^3\ g^{-1}$, respectively). Moreover, it was also interestingly found that these CTS-added carbonaceous products possessed both acidic (−COOH) and basic ($-NH_2$) groups on their surfaces. Taking the advantages of large surface area and −COOH/$-NH_2$ bifunctional surface, the carbonaceous nanomaterials exhibited excellent performance for adsorptions of cationic compound (i.e., methylene blue) at pH 10 and anionic compound (i.e., acid red 18) at pH 2, respectively. This work not only provides a simple and green route to prepare acid/base bifunctional carbonaceous nanomaterials with large surface area but also well demonstrates their potential for application in adsorption.

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1. Introduction

The wide applications of carbonaceous materials in the fields of adsorption, separation, and catalysis have stimulated an unfailing interest in developing efficient methods to produce such materials. Over the past several decades, the major strategies for preparation of carbonaceous materials are based on high-temperature carbonization (>400 °C), chemical vapor deposition, or laser ablation [1]. Admittedly, however, the accessibility and sustainability of those procedures are somewhat limited.

In recent years, much attention has been attracted to the preparation of carbonaceous materials according to the hydrothermal carbonization (HTC) process: thermal treatment of water mixed with carbohydrates (e.g., glucose, sucrose, or cellulose) at low temperature (e.g, 160–200 °C) [2–4]. The HTC method has the

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unique advantages of being very cheap, mild, and "green" as it involved no organic solvents, catalysts, or surfactant [5]. Moreover, such HTC-derived carbon nanoparticle (HCNP) possesses numerous oxygen-containing groups (e.g., −COOH and −OH groups) on its surface so that it can be effectively used as an adsorbent for the purposes of concentration (enriching) and removal (stripping) [6].

As widely reported, however, the HCNP generally exhibited a particle size between 0.2 and 1.5 μm and a specific surface less than 15 $m^2\ g^{-1}$ [1,7,8]. The low surface area of the HCNP largely limited its applications, although some strategies have attempted to enhance the surface area of HCNP by adding some removable templates or replacing the solvent (i.e., H_2O) with ionic liquids [1]. Thus, it is still highly desirable to develop more facile, environmentally friendly, and effective method for fabrication of large-surface-area HCNP.

On the other hand, these −COOH and −OH groups on the surface of HCNP are capable of capturing cationic molecules or ions but nearly powerless to adsorb anionic species [9]. Surface terminated with $-NH_2$ groups can make HCNP positively charged in acidic conditions and thus enhance its adsorption capacity for anions [9]. Up to date, however, only two reports have been published about the surface modification of HCNP by $-NH_2$ groups [9,10]. Wang and co-workers fabricated an amino-functionalized HCNP by an HTC approach with ammonia in the precursor solution, and further demonstrated its adsorption performance for $Cr_2O_7^{2-}$ [9]. Using a similar procedure, Zheng and co-workers also obtained an HCNP containing $-NH_2$ groups residing on its surface, and further investigated its reducibility of transforming Ag^+ to Ag [10]. Unfortunately, the reported methods suffered from the obvious drawback of using environment-unfriendly reagent (i.e., ammonia) as reactant. Moreover, both research groups paid attention to the study on the utilization of basic groups (i.e., $-NH_2$), but they did not further clarify the existence of acidic groups (i.e., −COOH) on the surface of HCNP.

In the present work, we proposed a one-pot, mild, and environment-friendly method, i.e., thermal treatment (180 °C; 18 h) of glucose−water solution in the presence of chitosan (CTS), with the aim of preparing large-surface-area and acid/base (−COOH/$-NH_2$) bifunctional HCNP samples. The CTS, composed of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units (Fig. 1), is known to be a "green" (i.e., non-toxic and biocompatible) and very cheap polysaccharide [11,12]. Amino groups of CTS, especially, are attractive for several adsorption-related applications, including CO_2 capture, removal of anionic species or as binding sites for bioactive molecules, controlled drug release, and so on [13,14]. Our results demonstrated that the addition of CTS could significantly reduce the size of HCNP while introducing−NH_2 groups onto the surface of HCNP; at the same time, abundant −COOH groups were also formed on the surface of HCNP due to the evolution of C−OH groups of glucose and CTS [6]. As a consequence, the HCNP samples displayed a fascinating feature, that was, an acid/base (−COOH/$-NH_2$) bifunctional surface with large surface area (up to 254 m2 g^{-1}) (Fig. 1). To examine the availability of HCNP samples acting as dual-use adsorbents that could be used not only for capturing cationic compound but also for adsorption of anionic compound, we selected methylene blue (MB) and acid red 18 (AR18) as the cationic and anionic model compounds [15,16], respectively, and thoroughly investigated the kinetics, equilibrium, and thermodynamics regarding the adsorptions of MB and AR18 on the HCNP samples (Fig. 1).

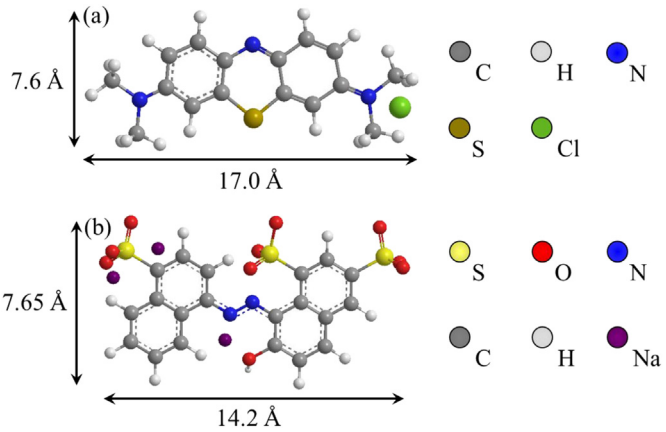

Fig. 2. Molecular structures and dimensions of MB (a) and AR18 (b).

2. Materials and methods

2.1. Chemicals and reagents

Chitosan (CTS, $M_w \cong 1000$, deacetylation degree > 90%) was purchased from Yuhuan Shell Biological Agents Factories (Zhejiang, China). Glucose, methylene blue (MB), and acid red 18 (AR18) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). As shown in Fig. 2a, the MB has a dimension of 1.70 nm (length) × 0.76 nm (width), and the area of MB molecule is therefore about 1.29 nm^2 [17]. The AR18 has a dimension of 1.42 nm (length) × 0.765 nm (width), and the area of AR18 molecule is about 1.09 nm^2 (Fig. 2b) [14]. All chemicals were used as received.

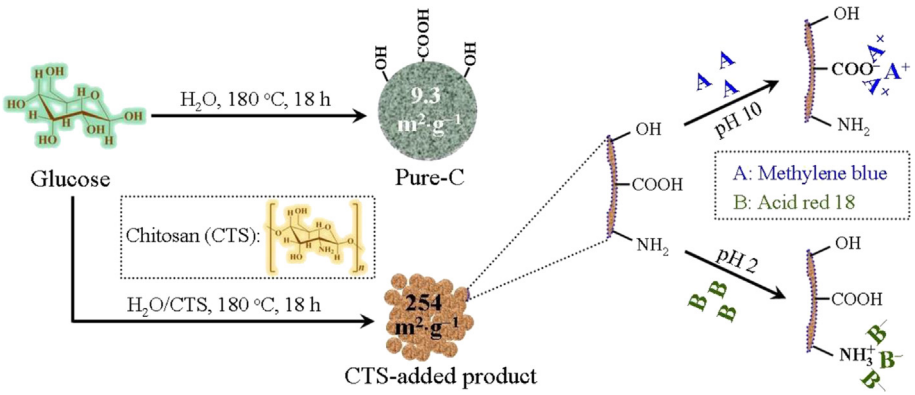

Fig. 1. The preparation of −COOH/$-NH_2$ bifunctional carbonaceous material and its performance for adsorptions of methylene blue and acid red 18.

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