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A facile approach to prepare porous cup-stacked carbon nanotube with high performance in adsorption of methylene blue

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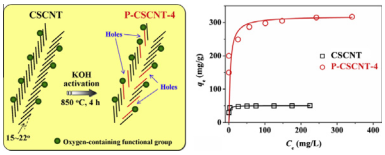
GRAPHICAL ABSTRACT



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ABSTRACT

Novel porous cup-stacked carbon nanotube (P-CSCNT) with special stacked morphology consisting of many truncated conical graphene layers was synthesized by KOH activating CSCNT from polypropylene. The morphology, microstructure, textural property, phase structure, surface element composition and thermal stability of P-CSCNT were investigated by field-emission scanning electron microscope, transmission electron microscope (TEM), high-resolution TEM, N_2 sorption, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy and thermal gravimetric analysis. A part of oblique graphitic layers were etched by KOH, and many holes with a diameter of several to a doze of nanometers connecting inner tube with outside were formed, which endowed P-CSCNT with high specific surface area ($558.7\ m^2/g$), large pore volume ($1.993\ cm^3/g$) and abundant surface functional groups. Subsequently, P-CSCNT was used for adsorption of methylene blue (MB) from wastewater. Langmuir model closely fitted the adsorption results, and the maximum adsorption capacity of P-CSCNT was as high as 319.1 mg/g. This was ascribed to multiple adsorption mechanisms including pore filling, hydrogen bonding, π–π and electrostatic interactions. Pseudo second-order kinetic model was more valid to describe the adsorption behavior. Besides, P-CSCNT showed good recyclablity and reusability. These results demonstrated that P-CSCNT had potential application in wastewater treatment.

1. Introduction

Nowadays, synthetic dyes are widely used in leather, paper, rubber, cosmetics and other industries. Dye-containing wastewaters are highly visible, since a very low concentration of dye in water is highly colored. Some of these dyes are toxic, mutagenic and cancer inducing, which invariably have negative impacts on the environment [1]. Thereby, it is of great importance to remove synthetic dyes from industrial effluents prior to their discharge, considering their long-term environmental toxicity and the potential for short-term damage to public health. Among various methods [2–5], adsorption has been one of the most common techniques because it is low cost, high efficiency, and easy and safe to perform [6,7]. A wide variety of adsorbents, including activated carbon [8–10], ordered mesoporous carbon [11], clay [12], silica [13] and graphene/Fe_3O_4@C [14], have been employed for the purpose of dye removal from wastewater.

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In recent years, carbon nanotubes (CNTs) have shown great potential in the application of environmental remediation [15–18]. It was reported that CNTs were more efficient in the removal of dioxins than activated carbon [19]. Owing to their unique tubular structure, large aspect ratio, good thermal and chemical stabilities, and good mechanical property, CNTs have been proven to possess huge potential as superior adsorbents for removing synthetic dyes [20–22]. Nevertheless, the performances of CNTs are far from satisfactory for many specific applications, and they usually suffer from slow adsorption rate or limited adsorption capacity due to their low specific surface area (compared to activated carbon), small pore volume and hidden pores inaccessible to adsorbate molecules, which prevent them from the large-scale application in wastewater treatment. Accordingly, modification must be conducted to improve their properties, and CNTs with characteristics such as fast adsorption rate and high adsorption capacity are thus highly expected.

As we know, the adsorptive property of adsorbent depends on the specific surface area, internal porous structure, and chemical/physical structure of the surface, since the properties of adsorbent surfaces and the types of interaction between adsorbate and adsorbent surfaces essentially control the adsorption at the solid/liquid interfaces. So far, a great deal of effort has been made to the physical or chemical modification of CNTs to obtain higher adsorption capacity and faster adsorption kinetics. They can be roughly classed into three strategies. The first strategy is physical or chemical activation of CNTs using acid (such as H_3PO_4, HNO_3 and H_2SO_4) [23–26], alkali (such as KOH) [16], metal oxide (such as Co_3O_4) [27], or other reagents to etch the surface graphitic layers, which facilitates the formation of pores and introduces surface functional groups. However, the conjugated skeleton of CNTs will inevitably be destroyed and the strong π–π coupling/stacking interaction between CNTs and aromatic rings of adsorbate will be weakened, which limit the improved adsorption capacity of CNTs. Besides, pores are generated only on the surface, the specific surface area is not enhanced remarkably, and the hollow structure of CNTs is still not utilized to accommodate more adsorbate molecules. The second strategy is the surface functional modification of CNTs by introducing functional materials such as polyaniline [28] and poly(sodium 4-styrenesulfonate) [29], which provide more adsorption sites on the external walls of CNTs and/or strengthen the interaction between CNTs and adsorbates. However, to a great degree, CNTs just act as support of the functional materials, and the advantages of CNTs such as large hollow structure and small size are always ignored. The third strategy is to cut down or scissor CNTs by ball mixing or using strong oxidizing agent, which promotes the formation of more edges (or even the transformation into graphene) and the migration of adsorbate molecules into the inner tube of CNTs. Unfortunately, the tube structure with a large aspect ratio will be lost. Hence, the investigations to improve specific surface area, utilize hollow structure, enhance pore volume and introduce functional groups for CNTs with a large aspect ratio are extremely desirable to significantly improve adsorption rate and adsorption capacity.

In this work, we used a novel type of CNTs, called cup-stacked CNTs (CSCNTs), with special stacked morphology consisting of many truncated conical graphene layers [30], which are much different from conventional CNTs made up of multi-seamless cylinders of hexagonal carbon networks. Such a special microstructure provides a large portion of exposed and reactive edges with abundant dangling bonds on the outer surface and in the inner channel of CSCNTs [31]. As a consequence, the utilization of these edges to surface modification or chemical functionalization has made them excellent candidates in the fields of nanoelectronics [32], composites [33], energy [34,35], electrochemical biosensors [36], and heterogeneous catalysis [37]. However, to the best of our knowledge, there are only two reports focused on the adsorption property of CSCNTs. Andrade-Espinosa et al. found that acid treatment improved the adsorption capacity of CSCNTs for Cd(II) by introducing more oxygen-containing surface functional groups [38]. In our previous report [39], CSCNTs were treated by HNO_3 oxidation and the enhanced adsorption capacity for methylene blue (MB) by CSCNTs was observed, which was ascribed to the π–π and electrostatic interactions between CSCNTs and MB. However, acid treatment in both studies could not obviously improve the specific surface area nor pore volume, as a result, the adsorption capacities of CSCNTs for Cd(II) and MB could not be enhanced remarkably, just similar with the case of conventional CNTs as mentioned earlier.

Herein, for the first time, KOH activation was demonstrated to simultaneously improve specific surface area, utilize hollow structure, enhance pore volume, and introduce functional groups for CSCNTs. After KOH activation, a part of oblique graphitic layers of CSCNTs were etched, the surfaces were spitted up, and many holes with a diameter of several to a doze of nanometers connecting inner tube with outside were formed. As a result, porous CSCNT (P-CSCNT) with high specific surface area (558.7 m^2/g), large pore volume (1.993 cm^3/g) and abundant surface functional groups was produced. P-CSCNT was then used for adsorption of MB from wastewater, and the adsorption isotherms and kinetics were studied. Langmuir model closely fitted the adsorption results. The maximum adsorption capacity of P-CSCNT was as high as 319.1 mg/g. Pseudo second-order kinetic model was more valid to describe the adsorption behavior. More importantly, P-CSCNT showed good recyclablity and reusability.

2. Experimental part

2.1. Materials

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) in analytical purity and used without any further purification. All solutions were prepared using deionized water. CSCNT with an average diameter of 57 ± 7 nm and an average length of 5 ± 2 μm was synthesized from polypropylene according to our previous work [39]. The P-CSCNT was prepared by activating CSCNT using KOH as depicted in Fig. 1. Typically, 5.00 g of CSCNT was mixed with KOH powder at a weight ratio of 1/6 and chemically activated at 850 °C for 2 h (or 4 h) under Ar atmosphere. The resultant mixture was washed with 15 wt% HCl solution, rinsed severally with distilled water until pH 6–7 was attained, and finally dried at 120 °C for 12 h to obtain 3.51 g of P-CSCNT-2 (or 2.86 g of P-CSCNT-4).

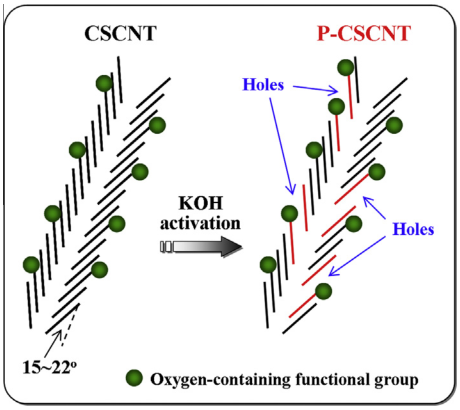

Fig. 1. Schematic illustration of the synthesis process of P-CSCNT by activating CSCNT using KOH.