

Room Temperature Amine Surface Modification of Synthesized Microporous Carbon Spheres

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Abstract: Carbon spheres (CSs) were hydrothermally synthesized using sucrose as precursor. The synthesized CSs were activated with potassium hydroxide (KOH) until a substantial micropore structure was achieved. The surfaces of the microporous carbon spheres (MCSs) were further modified with amine groups at room temperature using 3-aminopropyltriethoxysilane (3-APTES). Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Nitrogen Adsorption measurements were used to characterize the CSs, MCSs and the reaction product of MCSs with 3-APTES (3-APTES-MCSs). Results indicate the presence of Si-O-Si and -NH₂ groups on the surfaces of the 3-APTES-MCSs. The surface modified product can be utilized as an adsorbent for the extraction of nitrogen-containing contaminants of emerging concern (CEC) from environmental samples.

Keywords: Microporous carbon spheres, hydrothermal reaction, 3-aminopropyltriethoxysilane, sucrose, surface modification

1. Introduction

Carbon sphere (CS) is a simple word that is generally referred to carbons with a spherical or closely spherical structure. These materials are held together by Van der Waals forces which result into agglomerated collections of the materials. The discovery of spherical carbon materials has received much attention due to their controllable sizes, minimal surface energy, morphologies, and chemical properties [1]. Carbon materials having sphere shape have become familiar for the past years and their properties have been employed in

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different areas including tires, batteries, printer inks and etc. [2]. These types of spherical carbon materials have been designated with different names including carbon balls, carbon microbeads, carbon monospheres, carbon blacks, mesoporous microbeads, onions etc. Different techniques mainly high temperature pyrolysis, chemical vapour deposition [3], hydrothermal treatment [4], arc discharge [5] have been employed in the synthesis of carbon spheres and the mechanism through which carbon sphere is formed has been universally proposed and this depends on several factors which include reaction conditions, type of carbon precursor, presence or absence of catalyst [1].

In recent times, a great interest is indicated on the synthesis, activation and surface modification of carbon spheres. Current synthetic techniques have given rise to spheres with diverse range of sizes and surface properties. Some findings were published in literature related to the synthesis, activation and modification of carbon spheres [1,6]. A wide range of carbon sources have been used to make CSs. These sources vary from methane to glucose and include PAHs, carbon oligomer and polymers. Typically the carbon source is polymerized at high temperature and in the process smaller molecules such as water, carbon monoxide and carbon dioxide are eliminated. The sphere surface is non-ideal and consisted of graphite flakes that contain functional groups like COOH, OH, and others which can be converted or modified into other organic functional groups by conventional chemistry procedure [1].

Most amine surface modification of carbonaceous and silicate material reported in the literature were carried out at reaction temperatures ranging from 70°C to 75°C [7,8]. This work therefore focuses on the room temperature surface modification of MCSs using 3-APTES to generate amine modified MCSs (3-APTES-MCSs), and to propose possible applications of the modified material.

2. Materials and Methods

ACS reagent grade sucrose (99.5%) was obtained from Sigma-Aldrich (EMD Chemicals, Burlington, Canada). The KOH used was obtained from Merck (Darmstadt, Germany). All other reagents involved in this work were of analytical grade and used without further purification. 3-aminopropyltriethoxysilane with purity of 99% Aldrich (Dow Corning Corp. USA) was used as the functionalization agent. High purity deionized water of at least 18 M Ω was prepared by a Millipore water purification system (Molsheim, France).

Synthesis of Microporous Carbon Spheres

The MCSs used in this study were synthesized through hydrothermal reaction of sucrose to produce CSs followed by chemical activation of the CSs with KOH as described in our previous work [9].

Surface Modification of MCS

Approximately 0.03 g of dried MCS was mixed with 1.5 mL of 10% v/v 3-APTES/toluene solution in a sample vial. The sample vial was covered with a multi-pored aluminium foil and stirred at room temperature using a magnetic stirrer until the toluene is completely expelled. The resulting paste-like product was further dried at 110°C overnight and a powdered material recognized as amine-modified microporous carbon spheres was obtained. The experiment was repeated using 15% v/v 3-APTES/toluene solutions.

Characterization

The morphologies of both CS and MCS were determined on a Jeol JSM-6390LV scanning electron microscope (SEM) and JEOL-JEM-2100 transmission electron microscope (TEM). The Brunauer-Emmett-Teller (BET) surface area of each sample was measured using N₂ adsorption-desorption isotherms at degassing temperature of 110°C using metrometrics ASAP 2010 surface area analyser (Georgia, USA). The surface functional groups before and after 3-APTES modification of MCS were determined using version 5.3 Perkin Elmer Fourier Transform Infra-red (FTIR) spectrometer (Massachusetts, USA).

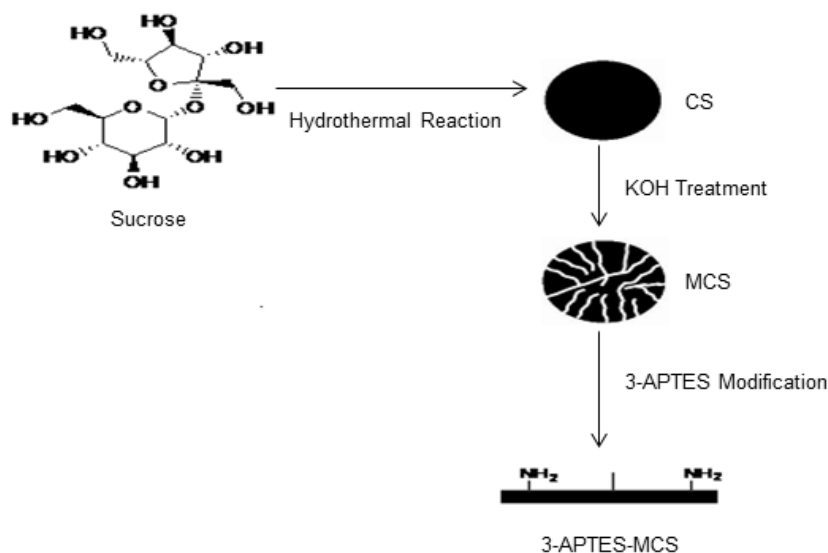


Fig. 1 Schematic representation for the synthesis of amine surface modification of microporous carbon spheres

3. Results and Discussions

Effects of KOH Activation and 3-APTES Modification on Surface Area and Pore Size

Evidences from our previous work [10] indicated that activation of CS using 2.0 mol/L KOH solution yielded a product that is more microporous in nature than with other tested KOH concentrations. Therefore

in this work, the CS was activated with 2.0 mol/L KOH and modified with 3-APTES. Table 1 summarizes the textural properties of CSs, MCSs and 3-APTES-MCSs. It is observed from the table that the surface area of MCS (308.1 m²/g) is far greater than that of CS (7.9 m²/g) indicating the formation of more pores on the CS during KOH activation as indicated on the magnified TEM images in Figures 2(a) and (b). After modification, the surface area and the micropore volume of 3-APTES-MCSs showed a decrease compared to MCSs (from 308.1 - 200.1 m²/g and 0.1 - 0.08 cm³/g respectively) which could be due to pore channels blockages by some of the functionalizing groups [11]. Comparing MCSs with 3-APTES-MCSs, no significant change in pore size was observed and this indicates that the functionalizing process does not play any obvious role in pore swelling of the MCSs.

Table 1 Textural properties of CS, MCS and 3-APTES-MCS.

Sample	BET surface area (m ² /g)	Micropore area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Pore Size (Å)
CSs	7.9	NA	0.009	NA	44.9
MCSs	308.1	258.4	0.133	0.10	17.2
3-APTES-MCSs	200.1	166.4	0.106	0.08	18.2

N.A = Not available.

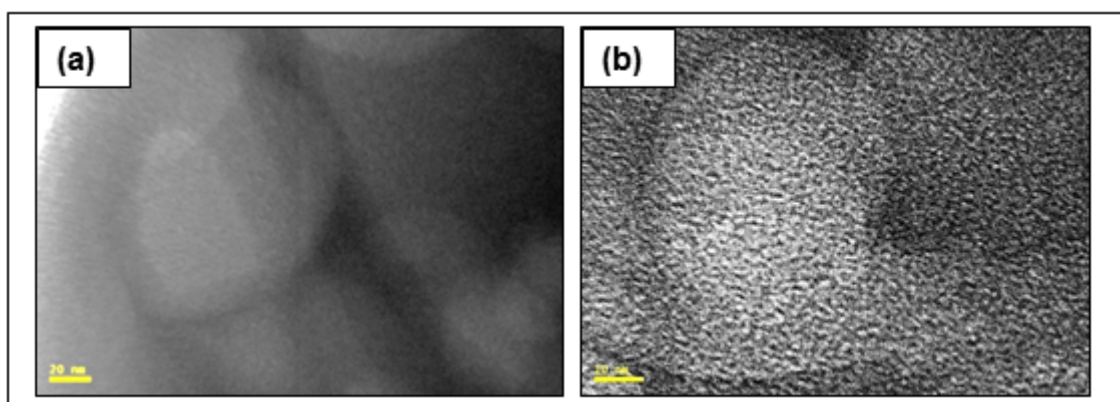


Fig. 2 Magnified TEM images for CSs (a) and MCSs (b)

Effects of KOH Activation and 3-APTES Modification on the Morphology

The morphological characteristics of CSs, MCSs and 3-APTES-MCSs were observed using SEM as

shown in Figure 3(a-c). Monodispersed carbon spheres with smooth outer surfaces were obtained after the hydrothermal synthesis (Fig. 3a). It is also noticed that the carbon spheres still retained their spherical shapes after KOH activation although the surfaces became slightly rough (Fig. 3b). The rough surfaces observed with MCSs could be due to some decomposition on the carbons during the activation process. No further distortion on the surfaces of MCSs was observed after 3-APTES modification (Fig. 3c) and this infers that the MCSs are strong enough to contain the modification process.

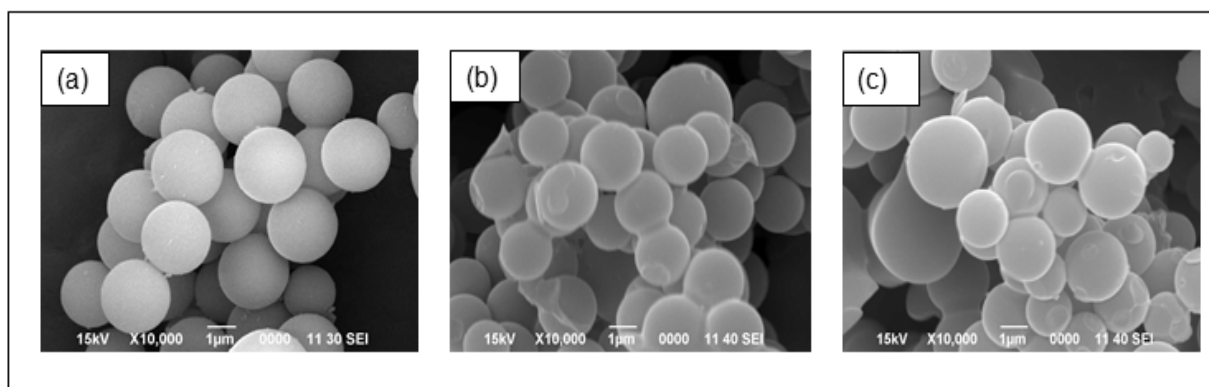


Fig. 3 SEM micrographs for CSs (a), MCSs (b) and 3-APTES-MCSs (c)

Infrared Spectra of CSs, MCSs, and 3-APTES-MCSs

Figure 4 provides the FTIR spectra for CSs, MCSs and 3-APTES-MCSs. The CSs and MCSs spectra (spectra a and b) are very similar to each other probably because the activation procedure did not significantly change the structure of the CSs. The strong and broad band at 3789 and 3350 cm^{-1} are attributed to the presence of hydroxyl groups (-OH) on the surfaces of the CSs, which presumably resulted from atmospheric moisture. This indicated that a large number of -OH groups are found on the surfaces of CSs. Two other bands appeared at 2923 cm^{-1} and around 1620 cm^{-1} giving information on C-H groups and C=C groups respectively which is consistent with Deshmukh and co-workers where they reported that CS shows two major sets of bands, one around 1630 cm^{-1} and the other between 2850 cm^{-1} and 2920 cm^{-1} indicating C=C and C-H groups respectively [1].

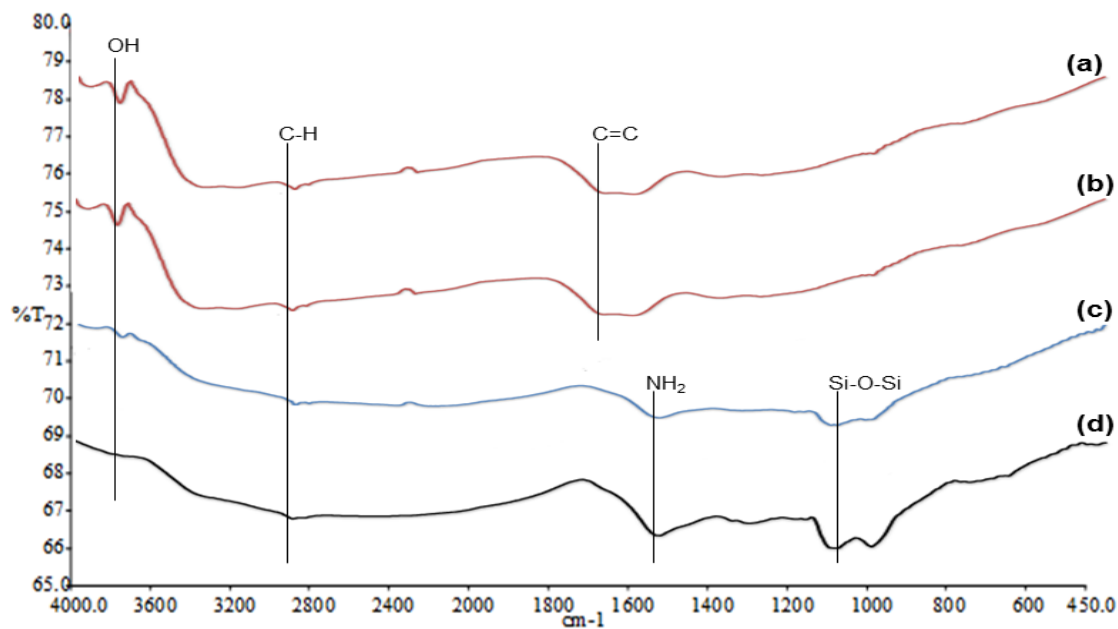


Fig. 4 FTIR spectra for CS (a), MCS (b), 3-APTES-MCS (c and d)

The FTIR spectrum of 3-APTES-MCSs modified with 10% v/v APTES/Toluene solution is shown in Fig. 4(c), a decrease in the intensity of -OH band and appearance of new band at 1117 cm⁻¹ were observed. The decrease in -OH intensity could be due to the reaction of -OH groups with the silanol groups to produce Si-O-Si at 1117 cm⁻¹. When the modification was carried out with 15% APTES/Toluene v/v solution (Fig. 4d), disappearance of the -OH groups was noticed and an increase in the intensity of the Si-O-Si is observed. This has confirmed our assertion that the -OH groups react with silanol groups to form Si-O-Si. The band at 1558 cm⁻¹ in spectra c and d are assigned to NH₂ scissors frequencies [12].

4. Conclusions

Amine surface modification of microporous carbon spheres was carried out at room temperature using 3-aminopropyltriethoxysilane. The morphology, surface area and attachment of the amine groups onto the surfaces of MCSs were confirmed by SEM, N₂-adsorption and FTIR analyses. It is envisaged that the synthesized amine surface bonded microporous carbon spheres will exhibit high extraction efficiency towards nitrogen-containing contaminants of emerging concern (CEC) due to their porous nature and more importantly the presence of amine groups which gives rise to chemical similarities between the adsorbent and analytes of interest. The focus of our future work is to apply the amine functionalized MCSs as adsorbent in solid phase membrane tip extraction of nitrosamines from water samples. The outcome of this

approach will then be compared with our previous work in which a non-modified MCS was used. This will enable us to assess the extraction efficiency of the modified adsorbent material. The application may be extended to include other nitrogen-containing contaminants.

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