

Hydrothermal Synthesis of Uniform Porous Carbon Nanospheres and their gas storage capacity

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ABSTRACT

We investigated the synthesis of porous carbon nanosphere via two-steps process, using phenolic resol as a carbon source and block copolymer F127 as a soft template via hydrothermal process followed by carbonization. The porous nanospheres have high surface area of 1619 m²/g after KOH activation measured by nitrogen sorption isotherms. The uniformity in the size of the nanospheres was verified by SEM and TEM analyses. The KOH activated porous carbon nanospheres show H₂ uptake of 2.42 wt.% (1 bar at 77K) and CO₂ adsorption capacity of 6.38 mmol/g (1 bar at 273K). The results indicate that this carbon material should have a high potential as gas adsorption carbonaceous materials.

Keywords: carbon spheres, nano materials, gas adsorption

1 INTRODUCTION

Due to depletion of fossil fuels and other environmental issues, developments of green energy materials are strongly demanded. Abundant gases such as carbon dioxides (CO₂) and hydrogen (H₂) are gaining considerable attention as an alternative potential energy source. With increasing environmental policy issue, CO₂ capturing can not only control the greenhouse gas emission from fossil fuel power plants, but also these captured CO₂ can be recycled by converting into useful products. Moreover, exhaust gases in hydrogen-powered applications will not contain any harmful-gases.

For aforementioned reasons, porous nanomaterials have been actively researched over the past decades due to its number of benefit from advantageous potential applicability in energy storage, adsorption, catalysis, supercapacitors, and biomedical applications [1-3]. Among the various candidates, carbonaceous materials including amorphous carbon, CNT and graphene have been considered due to their good thermal and chemical stabilities, mass production, and physical characteristic of light weight. However, the adsorption properties are greatly influenced by the porous network, pore size distribution, shapes and volume of void space within the material [4].

For these reasons, particular attention are being focused on controlling and manipulating the size, shape and

uniformity of the pores. Also, number of studies have reported that the morphology is also a crucial factor for some applications [1].

With growing interest in designing porous nanomaterials, various synthetic approach such as hydrothermal [5], template [5, 6], sonication [7] methods have been developed to synthesize spherical nanomaterial, as it has revealed superior performance in the range of applications [8]. Above all, hydrothermal polymerization process using carbon source such as glucose or phenolic resins with soft or hard templates followed by carbonization are now became one of the most general method. From the recent study, Fang et al. [9] have reported a simple hydrothermal approach based on the organic-organic assembly between phenolic resol as a carbon precursor and controlled low concentration of triblock copolymer (Pluronic F127) as a surfactant to produce ordered mesoporous carbon nanospheres, during carbonization step. The open mesopore size was estimated around 3.0 nm with BET specific surface area of 1131 m²/g.

Furthermore, in terms of gas adsorption properties, many study has revealed that nitrogen doping of carbons can enhance the surface properties due to polarity, electric conductivity, and electron-donor affinity [10], where recent study from Wickramaratne et al. [10] has revealed that nitrogen doped porous carbon spheres synthesized using polymer spheres via hydrothermal reaction can uptake up to 6.2 mmol/g of CO₂. However, nitrogen source generally involves toxic precursors such as ammonia based organic solutions, which may limit some applications. Therefore, other approaches such as activation and doping with metal nanoparticles are also being considered for altering the physical and chemical properties of carbons.

Herein, we report the synthesis of porous carbon nanosphere via two-steps process using phenolic resol as a carbon source and block copolymer (Pluronic F127) as a soft template via hydrothermal polymerization followed by carbonization. The manipulation of porosity was further conducted using KOH activation at various ratios. It is shown that increasing KOH activation ratio between carbon nanospheres and KOH resulted increase of higher specific surface area up to 1619 m²/g with high H₂ and CO₂ uptake of 2.42 wt.% at 77K and 6.38 mmol/g at 273K, respectively, showing these carbon nanospheres with a high potential as gas adsorption materials.

2 EXPERIMENTAL

2.1 Materials

Phenol (bioXtra, $\geq 99.5\%$), formaldehyde solution (37 wt.%), sodium hydroxide solution ($\sim 0.1\text{M}$), and Pluronic F127 were all purchased from Sigma-Aldrich. All chemicals were used as received.

2.2 Synthesis of porous carbon nanospheres

Porous carbon nanospheres (CNS) were prepared through aqueous hydrothermal synthesis route described by Fang et al. [9] In general, 0.6 g of phenol, 2.1 ml of formaldehyde solution (37 wt.%) and 15 ml of (0.1 M) of NaOH aqueous solution were mixed and stirred at 70 °C for 30 minutes. Then, 0.96 g of F127 dissolved in 15 ml of distilled water solutions are added into the mixture and temperature was lowered to 66 °C for 2 hours followed by further addition of 50 ml of distilled water. During this reaction, stirring was adjusted to 340 rpm and colorless solution has transformed into pink and crimson. After 18 hours, reaction was stopped.

17.7 ml of mixed solution was transferred into autoclave and diluted with 56 ml of distilled water and heated at 130 °C for 24 hours. The obtained product was collected and washed with distilled water and freeze-dried for 12 hours. The carbonization was proceeded at 700 °C in N₂ atmosphere for 3 hours at rate of 5°C/min and CNSs were collected for further characterizations.

2.3 KOH activation of porous CNS

For KOH activation, prepared CNSs and KOH at ratios of 1:1, 1:2, 1:3, and 1:4 (wt.%) are hand mixed together and heated at 700 °C in N₂ atmosphere for 1 hour at rate of 3 °C/min. Activated CNSs were washed with distilled water then freeze-dried for overnight for further characterizations.

2.4 Characterization

Transmission electron microscopy (high-resolution TEM) measurements were conducted on a JEM-3000F microscope (JEOL, Japan) operated at 300 KV. Field emission scanning Electron microscopy (FE-SEM) images were recorded on Merlin Compact electron microscopy operating at 1KV with Pt coating. The nitrogen (N₂) and hydrogen (H₂) (at 77K), and carbon dioxide (CO₂) (at 273K and 298K) adsorption measurements were conducted on Belsorp-mini (BEL, Japan). Surface area was calculated using the Brunauer-Emmett-Teller (BET) method from nitrogen adsorption-desorption isotherm.

3 RESULTS AND DISCUSSION

3.1 Structure of porous CNSs

Figure 1 shows the SEM images of hydrothermally synthesized resins (Figure 1a), CNSs carbonized at 700°C for 3 hours in nitrogen atmosphere (Figure 1b), and its KOH activated CNSs with different ratio (Figure 1c to 1f). The obtained particles all possessed spherical morphology with almost uniform diameters. Moreover, the ordered mesostructures are also observed in the SEM images. It is interesting that even with increase of KOH activation ratio, the particles still remains its spherical morphology with slight of dent possibly due to surface activation by KOH treatment.

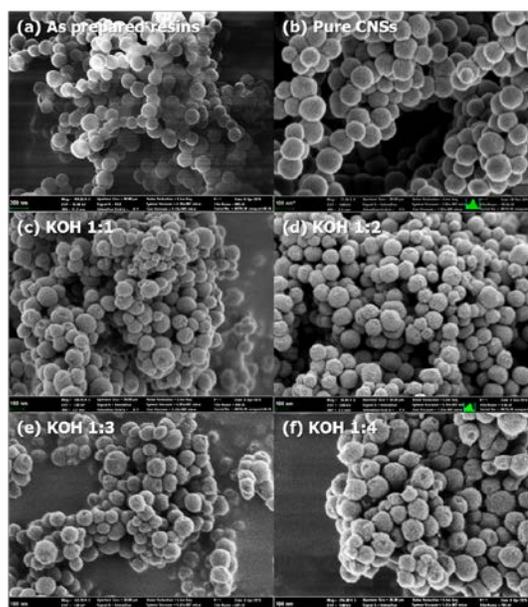


Figure 1 SEM images of (a) as-prepared, (b) pure porous carbon nanospheres (CNS), (c) 1:1 KOH activated CNS, (d) 1:2 KOH activated CNS, (e) 1:3 KOH activated CNS, and (f) 1:4 KOH activated CNS.

Figure 2 illustrates TEM images of hydrothermally synthesized resins (Figure 2a), CNSs carbonized at 700°C for 3 hours in nitrogen atmosphere (Figure 2b), and its KOH activated CNSs with different ratio (Figure 2c to 2f). Again, spherical morphology has been confirmed throughout all samples, but ordered mesoporous sites cannot clearly be observed in as-prepared sample (Figure 2a). This is because during the carbonization process, the template (F127) gets removed and opening the mesopores structured obtained during hydrothermal process [9].

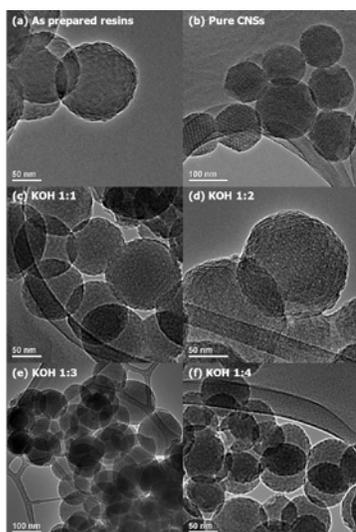


Figure 2 TEM images of (a) as-prepared, (b) pure CNS, and KOH activated CNS at ratio of (c) 1:1, (d) 1:2, (e) 1:3, and (f) 1:4.

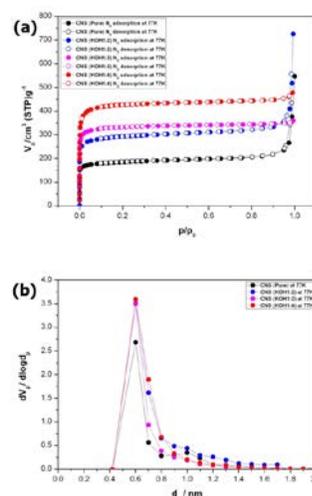


Figure 3 Nitrogen adsorption-desorption isotherms and pore size distribution measured at 77K for KOH activated CNSs at different ratios at 700 °C for 1 h in N₂ atmosphere.

3.2 Gas adsorption-desorption studies

We evaluated the porosity of pure CNSs and KOH activated CNSs using nitrogen adsorption-desorption isotherms at 77K and the corresponding pore size distribution curves, illustrated in Figure 3a. All adsorption isotherms shows type I of adsorption isotherm with slight H1 hysteresis loop at high relative pressure. This behavior is typically associated with micropores and mesopores. Moreover, with increase in KOH ratios, increment of N₂ adsorption properties can be observed indicating that KOH activation has successfully increased the surface areas CNSs.

The summarized adsorption parameters obtained by analysis of the experimental isotherms are provided in Table 1. The BET surface areas of pure CNSs is 691 m²/g, whereas, KOH activation at 1:4 ratio shows 1619 m²/g almost higher than twice of the pure CNSs. Although, the pore size distribution (Figure 3b) shows uniform micropore size of 0.6 nm throughout all pure CNSs and KOH activated CNSs samples, the area under the graph also confirms the increase in surface areas with higher ratios of KOH activation.

The H₂ and CO₂ adsorption performance of all samples was also examined and illustrated in Figure 4.

The summarized H₂ and CO₂ adsorption parameters obtained by analysis of experimental isotherms are also provided in Table 1.

The H₂ adsorption-desorption is shown in Figure 4a, where, pure CNSs only shows 1.60 wt.% of hydrogen uptake, whereas 1:4 KOH activated CNSs shows 2.42 wt.% of hydrogen measured at 77K. the higher surface area associated with KOH activation of CNSs lead to increased H₂ adsorption. Micropore size also contributes to increases in hydrogen uptake since KOH activation has etched the surface of CNSs producing smaller pore size.

The CO₂ adsorption-desorption at 273K (Figure 4b) and 298K (Figure 4c) are illustrated. Again, higher ratios of KOH activation shows higher adsorption of CO₂, where 6.38 mmol/g and 3.84 mmol/g of CO₂ adsorptions were measured for 273K and 298K, respectively. This is very interesting as, in general, N-doped porous carbon is known to be one of the most promising candidates for CO₂ adsorption [10]. However, in this study, there is no presence of nitrogen but just carbon. As, CO₂ adsorption is not limited by the total pore volume but only by pores smaller than a hydrothermal synthesis followed by carbonization and investigated their H₂ and CO₂ adsorption properties.

Table 1 Adsorption parameters for pure CNS and KOH activated CNSs obtained by analysis of the N₂, H₂ and CO₂ adsorption isotherms shown in Figure 4 and 5.

Samples*	S _{BET} /m ² g ⁻¹	V _{total} /cm ³ g ⁻¹	V _{micro} /cm ³ g ⁻¹	V _{meso} /cm ³ g ⁻¹	H ₂ uptake at 77K/wt.%	CO ₂ uptake at 273K/mmol g ⁻¹	CO ₂ uptake at 298K/mmol g ⁻¹
CNS700	691	0.9312	0.2918	0.0957	1.60	4.16	2.93
CNS700-2	1099	0.9404	0.4370	0.1147	1.87	5.40	3.61
CNS700-3	1253	0.5502	0.5024	0.0352	2.21	6.12	3.63
CNS700-4	1619	0.7376	0.6446	0.0560	2.42	6.38	3.84

* CNS700 denotes carbon nanospheres carbonized at 700 °C for 3 hours, CNS700-number gives the KOH ratios.

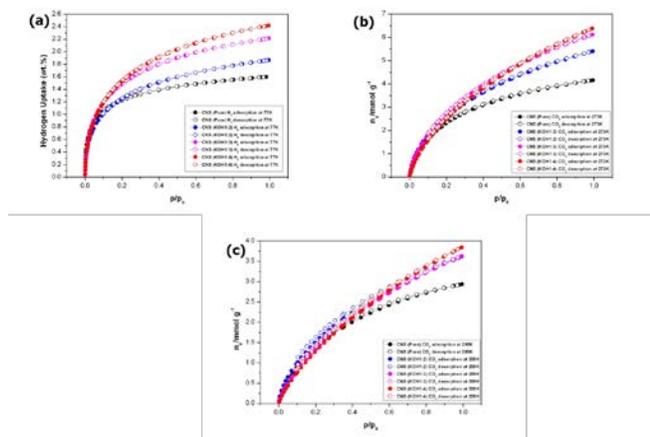


Figure 4 (a) H₂ uptake at 77K and CO₂ adsorption isotherms at (b) 273K and (c) 298 K for pure CNS and KOH activated CNSs with different ratios.

certain diameters [4], CNSs already having both micro-mesopores structures, KOH activation has not only increased the existing micropores volume but also has created more narrow micropores by reducing the mesopore volume, therefore increase in CO₂ adsorption.

4 CONCLUSIONS

In this study, we have produced KOH activated uniform porous carbon nanospheres using phenolic resol-F127 under It is interesting that even after KOH activation up to 1:4 ratios, the CNSs still remained its spherical morphology and increased its BET specific surface area up to 1619 m²/g but also increased the micropore volume up to 0.6446 cm³/g. The H₂ adsorption capacity can reach 2.42 wt.% at 77K, which is high value for spherical morphological carbon nanoparticles. Also, CO₂ adsorption capacity can reach up to 6.38 mmol/g and 3.84 mmol/g at 273K and 298K, respectively. This is very high value for carbon only substance as, in general, nitrogen doped porous carbon usually exhibits high uptake of CO₂, whereas CNSs produced in this study has no presence of nitrogen source. The study indicate that this porous carbon nanospheres should have a high potential as gas adsorption carbonaceous materials.

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