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Synthesis and characterization of Ni nanoparticles supported on nitrogen-doped mesoporous carbon

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Abstract. Nitrogen-doped mesoporous carbon (N-MC) was synthesized by the soft-templating method using phloroglucinol/formaldehyde and melamine as carbon and nitrogen precursors, respectively, and Pluronic F127 as a template for the generation of mesopores inside the carbon structure. Scanning electron microscopy analysis revealed that the material had a rough surface, while Raman analysis indicated the existence of sp^2-hybridized carbon rather than sp^3, similar to graphite. The increase of the D-band to G-band intensity ratio indicated that N-MC has a more graphite-like structure than pristine mesoporous carbon. X-ray photoelectron spectroscopy analysis confirmed that nitrogen was successfully doped into the carbon framework. The material was then used as a support for Ni nanoparticles (Ni-NPs). The presence of Ni metal in Ni-NP@N-MC was confirmed by X-ray diffraction analysis.

Keywords: mesoporous carbon, Ni nanoparticles, N-doped carbon, soft-templating method

1. Introduction

Industrial activity has steadily increased since the advent of the industrial revolution, leading to ever increasing emission of CO_2 into the atmosphere. Accordingly, the pre-industrial revolution atmospheric CO_2 concentration of 280 ppm has increased to its current level of 380 ppm [1]. This has become a serious environmental problem because of the contribution CO_2 makes to the greenhouse effect, leading to global climate change. Consequently, to reduce this negative effect, it is absolutely vital that we decrease the amount of anthropogenic CO_2 released into the atmosphere.

The current technology used for large-scale CO_2 absorption is based on liquid amine absorption [2, 3]. Amine groups can remove CO_2 from the air owing to their ability to reversibly form carbamate and bicarbonate compounds. However, this method suffers from disadvantages related to high energy consumption, corrosion, and solvent evaporation [4,5]. A potential strategy for overcoming these problems is the immobilization of the working amine compounds onto the surface of support materials instead of using them in the liquid state [6].

Since its initial development, mesoporous carbon has been used in a wide range of applications, including adsorbents [7], sensors [8], molecule carriers [9], and catalyst supports [10]. However, the use of mesoporous carbon in CO_2 adsorption is still limited as CO_2 is only weakly physisorbed on mesoporous carbon. Recently, our group successfully prepared mesoporous carbon modified with amine compounds [11,12]. The amine compounds were immobilized in the pores of the mesoporous carbon, enhancing its capacity to adsorb CO_2. However, the effect of nitrogen compounds with both sp^3 and sp^2 hybridization on the CO_2 sorption properties of mesoporous carbon remains largely unresearched. Accordingly, in this work, a mesoporous carbon framework was doped with nitrogen using melamine as a nitrogen source.
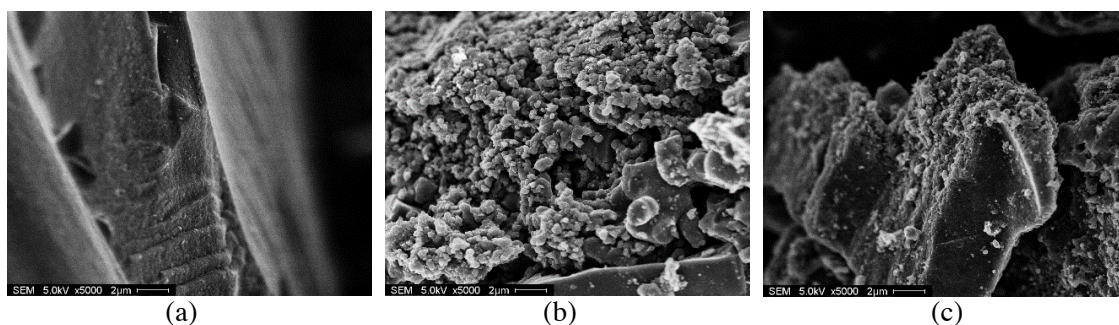
(a)   (b)   (c)

Figure 1. SEM images of (a) MC, (b) N-MC, and (c) Ni@N-MC (×5000)

2. Experimental

2.1. Synthesis of mesoporous carbon (MC)

Mesoporous carbon was synthesized using a previously reported procedure [13]. Briefly, phloroglucinol and Pluronic F127 were dissolved in an ethanol/water mixture. Then, 37% HCl was added, and the solution was vigorously stirred for 30 min. Under continuous stirring, formaldehyde (37%) was then added drop-wise to the solution, and then the mixture was stirred for another 30 min before being split into two layers. The bottom layer was removed and the stirring was continued overnight, before being transferred to an autoclave and cured for 24 h in the oven at 100 °C. The material was carbonized under nitrogen flow with a heating rate of 1 °C/min from 100 to 400 °C and 5 °C/min from 400 to 850 °C before kept at 850 °C for 2 h.

2.2. Synthesis of nitrogen-doped mesoporous carbon (N-MC)

In a typical synthesis, 1.25 g Pluronic F127 and 0.625 g phloroglucinol and were dissolved in a 9.7 g ethanol/water (10:9 *w/w*) solution. Once the solid had completely dissolved, 0.08 mL 37% HCl was added drop-wise, and the solution was stirred for 30 min (mixture A). Separately, 0.625 g melamine was dissolved in 26 mL water in a round-bottom flask, which was heated under reflux at 80 °C (mixture B). Then, 1.25 mL 37% formaldehyde was added to mixture A. After 5 min, mixture A was added slowly to mixture B and the solution was stirred for 30 more min until solid precipitate appeared. The solid was then filtered, washed with water, and dried in airy condition. It was then transferred to a 200 mL Teflon-lined stainless steeled autoclave and cured in an oven at 150 °C for 72 h. The material was carbonized under nitrogen flow with a heating rate of 1 °C/min from 100 to 400 °C and 5 °C/min from 400 to 850 °C before being kept at 600 °C for 2 h.

2.3. Impregnation with Ni nanoparticles (Ni@N-MC)

First, 0.5 g N-MC was dispersed in 10 mL water. Second, in separate flask, 1.23 g $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 5 mL of water, followed by being added drop-wise to the carbon dispersion. This mixture was stirred for 6 h, then the solid composite was filtered, washed with water, and dried in airy condition. The obtained solid and 20 mL ethylene glycol were transferred into a round-bottom flask for reflux treatment at 170 °C for 6 h. The final solid was then filtered, washed with water and ethanol, and dried in airy condition.

2.4. CO_2 adsorption

CO_2 and N_2 were introduced to the adsorbent at a flow rate of 20 cm^3/min each. The output CO_2 was dissolved in 0.1 M NaOH solution. The amount of CO_2 was then derived by titration against 0.1 M HCl with phenolphtalein and methyl orange as indicator.

3. Results and discussion

The morphologies of MC, N-MC, and Ni@N-MC were observed by scanning electron microscopy (SEM), as shown in figure 1. All the materials present rough surfaces. A grass-like structure is observed for the surface of MC, as has been previously reported [14]. This characteristic surface mor-
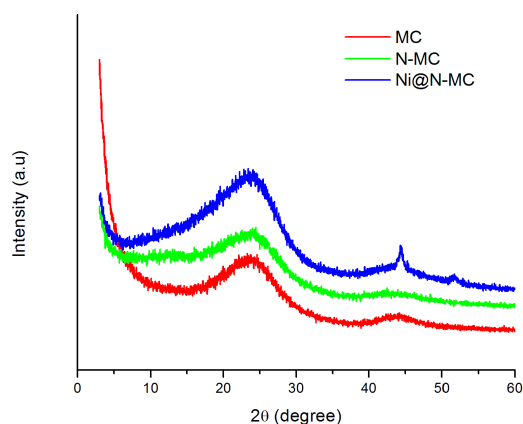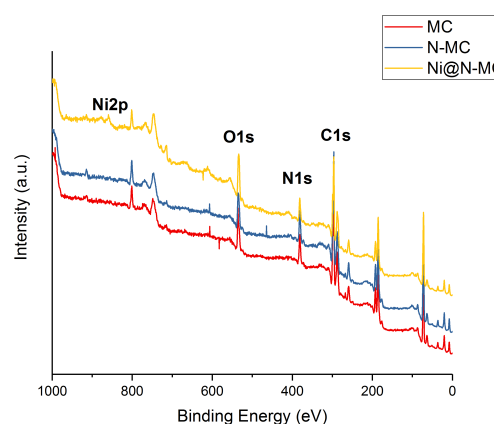
Figure 2. XRD pattern of MC, N-MC, and Ni@N-MC.

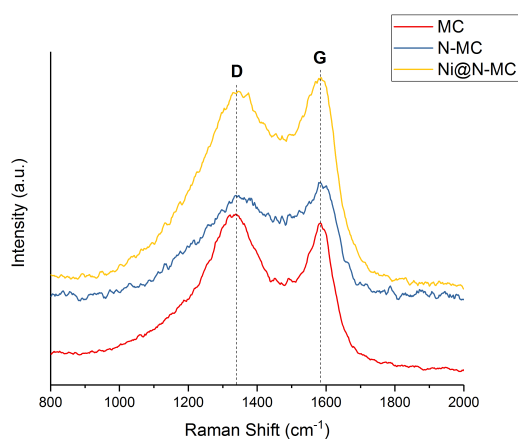**Figure 3**. XPS spectra of MC, N-MC, and Ni@N-MC.

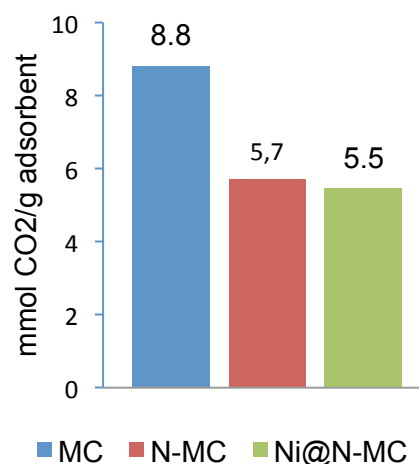**Figure 4**. Raman spectra of MC, N-MC, and Ni@N-MC.

Figure 5. CO_2 adsorption of MC, N-MC, and Ni@N-MC.

phology endows the MC with a high surface area. Both N-MC and Ni@N-MC exist as small particles. There is no observable difference in morphology upon impregnation with Ni nanoparticles.

Figure 2 shows the X-ray diffraction (XRD) patterns for MC, N-MC, and Ni@N-MC. It is clear that all the samples present very similar diffraction patterns. The peaks for $2\theta = 25°$ and $44°$ are attributed to the (002) and (101) planes, respectively, which are characteristic of graphitic carbon [15]. The similarity of the diffraction patterns indicates that there is no significant change in the structure of the material upon nitrogen doping. For Ni@N-MC, there are additional peaks at $2\theta = 45°$ and $52°$ owing to the presence of Ni metal [16]. This confirms the success of the Ni nanoparticle impregnation into the mesoporous carbon. The X-ray photoelectron spectroscopy (XPS) spectra (figure 3) further confirm the presence of Ni in addition to C, N, and O in Ni@N-MC.

The Raman spectra (figure 4) reveal Raman shifts at 1339 and 1584 cm⁻¹, which are the characteristic D-band and G-band, respectively, of graphitic materials. The spectral peaks for all the materials occur at the same frequency, indicating that the Raman spectra are not affected by nitrogen doping. However, the D-band to G-band intensity ratio (I_D/I_G) changes from 1.01 for MC to 0.98 for N-MC and Ni@N-MC. This indicates that nitrogen doping increases the abundance of sp² carbon relative to that of sp³ carbon.

The results for the CO_2 adsorption capacities of the materials are shown in figure 5. Although modification with amine compounds has been shown to increase the CO_2 uptake of mesoporous carbon

in previous works [11,12], modification with melamine as the nitrogen source decreases the CO_2 uptake of the N-doped mesoporous carbon. This is most likely due to structural shrinkage of the framework upon nitrogen doping and also the low primary and secondary amine contents, since the nitrogen forms bonding interactions with the carbon framework. Furthermore, the Ni nanoparticles in Ni@N-MC appear to have no significant effect on CO_2 adsorption. Ongoing work is underway in our group to determine the mesoporosity and basicity of these materials, which are important for further application as heterogeneous catalysts for CO_2 fixation reactions.

4. Conclusions
Nitrogen-doped mesoporous carbon was successfully synthesized using a soft-templating method with melamine as nitrogen source. The CO_2 adsorption capacity of N-MC is lower than that of MC. This may be due to structural shrinkage upon nitrogen doping and also the low primary and secondary amine contents. Nevertheless, this material has the potential to be employed as an alternative sorbent for CO_2 capture.

Acknowledgements

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