N-Doped porous carbon nanoflakes : Excellent adsorbent for low pressure CO_2 capture

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Abstract. Porous carbon is a promising research subject for CO_2 capture from post combustion process, direct air capture and recently for hydrogen fuel purification application. Apart from having unique surface area and pore morphology, they can be also be prepared from low cost materials through easy synthesis route. The tuning of their pore size and N heteroatom have also proven to robust its performance in previous studies. . Therefore a highly porous N-doped carbon nanoflakes from starch was prepared and its performance in CO_2 capture was studied. Among the samples, starch hybrid (SH800) exhibit good CO_2 capture capacity of 29.8 wt.% for biohydrogen gas adsorption at mild temperature and pressure. The sample also displayed distinct morphology of nanoflakes and carbon lattice in FESEM and XRD analysis. In summary, the sorbent is a potential material for biohydrogen CO_2 capture studies.

1. Introduction

The side-effect of fossil fuel combustion has led to the introduction of alternative energies such as solar, wind, tidal and recently fuel cell energy[1]. Currently, researchers have been investigating various methods to improve the performance of proton exchange membrane (PEM) fuel cell. One issue that is needed to be solved is the impurities in the fuel itself. Since PEM use reformed fuel as their fuel source, impurities such as carbon dioxide, nitrogen, carbon monoxide and trace amount of hydrogen sulfide always causes performance loss due to salts and byproducts corrosion. Since only 10-50 ppm of CO_2 is needed to cause low rate of hydrogen dissociation on membrane electrode assembly (MEA) catalyst, gas purification system need to be done to obtain 99.99% concentration of H_2 feed gas[2]. To date, various studies has been done for high and ultradilute concentration of CO_2, however less for biohydrogen gas application (40~50% CO_2).

Solid sorbent materials such as silica, metal organic framework (MOF) and zeolite are potential adsorbents for biohydrogen gas CO_2 capture[3–5]. Whilst a lot of efforts has been developed to impregnate amine rich source into these solid CO_2 adsorbent, performance loss still occur due to several factors. Such is unwanted adsorption isotherm, meanwhile the other is due to lacks of basis

group for CO_2 interaction. In some studies, chemical adsorption is also deemed as unpreferable for adsorption-desorption process to avoid unnacessary strong bond between CO_2 and adsorbent. This is why it is important to develop a porous materials with not only good pore structure, number and size but with good physiosorbent properties too. An example of material that possesed such properties is the conventional porous silica and recently, N-doped porous carbon.

Porous carbon morphology can be divided into three section; macroporous (>50nm), mesoporous (2-50nm) and microporous (<2nm). While researchers still debating the best pore size for CO_2 application, smaller pores are suspected as the better structure as long as there are high total surface area. At relatively low pressure, Wang and co-workers concluded that macroporous framework sorbent with extremely high microporosity and high surface area contribute to excellent CO_2 adsorption[6]. However, Ravi and co-workers discussed that mesopores are better than micropores since the latter causes pore blockage, especially during N-doping or activation[7]. In terms of N-doping, it is the current trend to increase the basicity of adsorbent since the nature of CO_2 is acidic. Based on previous studies, hydrogen bonding resulting from CO_2 and N-friendly neighbour H atom (pyridinic N) is responsible for a better CO_2 capture capacity. Herein, we prepare a versatile porous CO_2 adsorbent with optimal pore properties, high functional N group and CO_2 adsorption capacity, under mild pressure and temperature for biohydrogen gas application. The sample will be analysed by using FESEM, XRD and CO_2 screening analysis.

2. Materials & Synthesis

To summarize, starch, amine source and porogen were added under continuous strring. The resulting solution was then dried leaving a slurry solution and pyrolysed at desired temperature. Acid wash were then done before sonification with distilled water. The dried sample were named as SH800. For comparison, bare starch was pyrolised at 800 °C to produce control activated carbon named S800. Meanwhile, another control material were prepared by replacing starch in the preparation route of SH800 with melamine. The sample was named M800. Figure 1 summarize the flowchart of sample preparation route.

Figure 1. Summary of reparation route for sample SH800

3. Physical properties

The morphology of SH800 was evaluated using FESEM analysis. From Figure 2 (a,b), it is clear that SH800 exist as nanoflakes with good consistency. This suggests that activation temperature is an important parameter in this study. Interestingly, a higher temperature results in higher crystallinity of sample, which is supported through XRD analysis explained in further section of this paper.

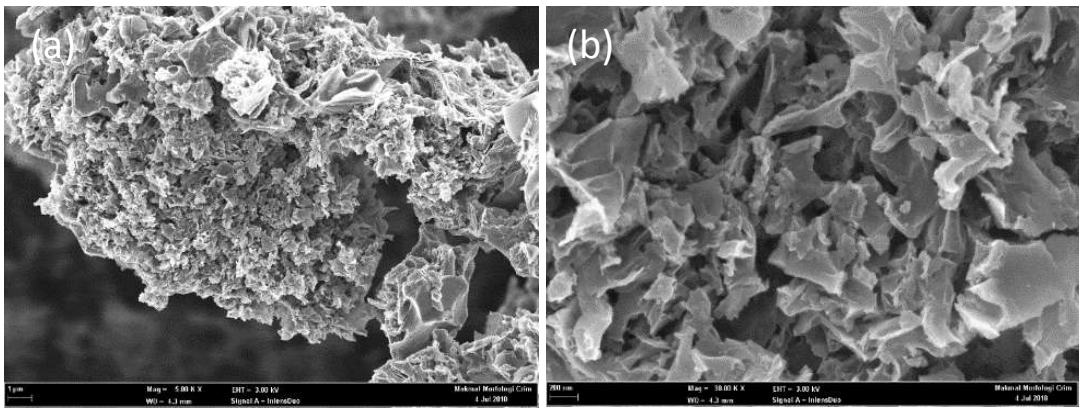

Figure 2. FESEM images of SH800 at 1 µm (a) and 200 nm (b)

4. Chemical Properties

As seen in Figure 3(a), the spectrum of SH800 was barely seen in FTIR analysis seen due to the dark color of sample powders. Distinctive peak can be seen at 824 cm^{-1}, meanwhile broad bands were located at 1203, 1560, 3314 cm^{-1}. These findings proves the existance of functional groups that is important for further CO_2 adsorption study. Figure 3(b) shows the wide angle XRD profile of SH800. The spectrum of SH800 displays sharp peak at 26.4° with interlayer *d*-spacing of 0.34 nm indexed as the (002) lattice planes of carbon. A broad peak with low intensity at 15° proves the existance of traces C_3N_4 as it corresponds to the in-plane structural packing motif indexed as (100) phase, as reportd by Liao and co-workers[8]. Since no residual peak of metal is seen, we can assume that no metal traces exist in the sample.

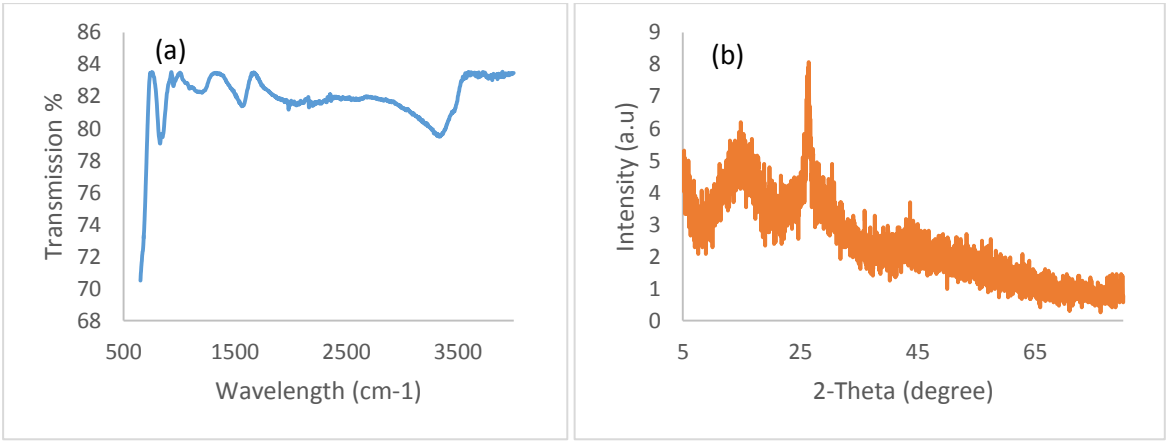

Figure 3. FTIR analysis of SH800 (a). XRD profile of SH800 (b)

For final analysis, the adsorbent was tested for CO_2 capture ability in low temperature and pressure. The test was set up as in Figure 4(a), and calculated by using equation (1) where the CO_2 capacity is the function of adsorption time at first 10 % of total CO_2 percentage captured. Figure 4(b) shows the capture capacity for different samples of M800, S800 and SH800. As seen from the Figure 4(b), sample SH800 displayed the highest adsorption capacity of 29.8 wt.%, followed than S800 and M800. This shows that N-doped porous carbon is a suitable material for CO_2 capture studies. Since direct air was used as desorption gas, the packing material is practical for real life application since N_2 gas is not needed. Thus the operating cost is reduced greatly.

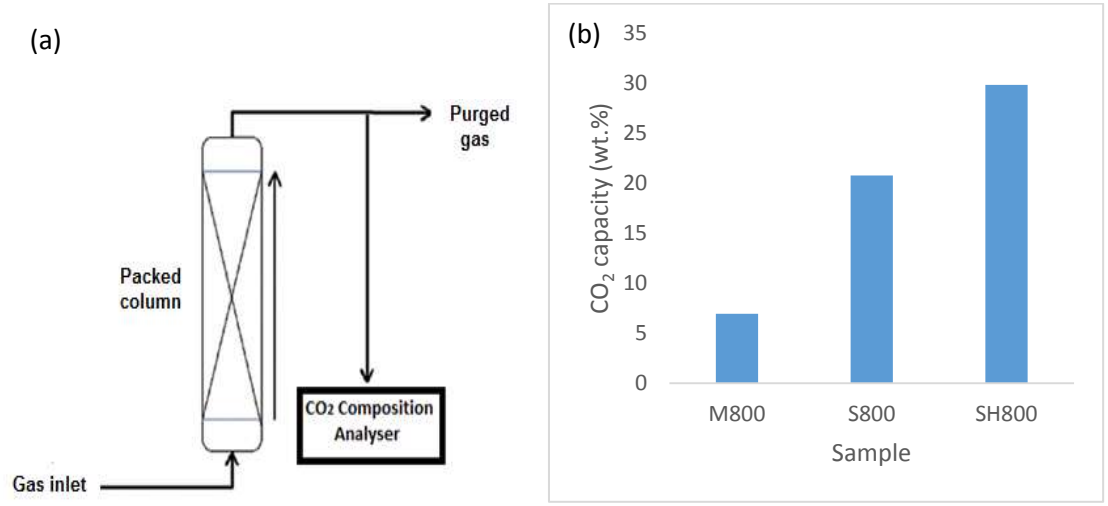

Figure 4. Gas adsorption set-up ilustration (a). CO_2 screening analysis of different samples (b)

$$\text{Adsorption capacity} = \frac{\text{Gas flow rate (L/min)} \times \text{Breakthrough time (min)} \times 44.01\,\text{g/mol}}{\text{Volumetric flowrate (L/mol)} \times \text{Adsorbent mass (g)}} \quad (1)$$

5. Conclusion

A N-doped porous carbon hybrid nanoflakes named SH800 was successfully prepared. The sample displayed distinctive nanoflakes morphology in FESEM analysis and carbon lattice in XRD analysis at 26.4°. It also displayed high CO_2 adsorption of 29.8 wt.%, excellent for adsorption study at mild temperature and pressure. To conclude, the prepared adsorbent SH800 is a suitable material for biohydrogen CO_2 capture applications.

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