



## Fast and Soft Functionalization of Carbon Nanotube with $-\text{SO}_3\text{H}$ , $-\text{COOH}$ , $-\text{OH}$ Groups for Catalytic Hydrolysis of Cellulose to Glucose

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### Abstract

Herein, sulfonated carbon nanotubes (CNT) have been prepared in dilute sulfuric acid ( $\text{H}_2\text{SO}_4$ ) via a novel sulfonation approach based on gas-liquid interfacial plasma (GLIP) at room temperature. The sulfonic acid groups and total acid groups densities of CNT after GLIP treatment in 2 M  $\text{H}_2\text{SO}_4$  for 45 min can reach to 0.53 mmol/g and 3.64 mmol/g, which is higher than that of sulfonated CNT prepared under 0.5 M / 1 M  $\text{H}_2\text{SO}_4$ . The plasma sulfonated CNT has been applied as catalysts for the conversion of microcrystalline cellulose to glucose. The effect of hydrolysis temperature and hydrolysis time on the conversion rate and product distribution have been discussed. It demonstrates that the total conversion rate of cellulose increasing with hydrolysis temperature and hydrolysis time. Furthermore, the GLIP sulfonated CNT prepared in 2 M  $\text{H}_2\text{SO}_4$  for 45 min has shown high catalytic stability of 85.73 % after three cycle use.

*Keywords* : Gas-liquid interfacial plasma, Soft sulfonation, Dilute sulfuric acid, Sulfonated carbon catalysts, Cellulose transformation

## 1. Introduction

Biomass resource has been regarded as a promising alternative to fossil fuel because its abundant reserves and environmental-friendly property [1,2]. In general plant fibers, microcrystalline cellulose accounts for about 70 %, and the amorphous fraction is about 30 % [3]. Microcrystalline cellulose is composed of glucose monomers connected by numerous 1-4 beta glycosidic bonds. In addition, large number of intramolecular and intermolecular hydrogen bonds are presented inside the cellulose structure [4]. Although conventional hydrolysis of cellulose to glucose with liquid acids generally exhibits good catalytic performance, the post separation of target reducing sugars with hydrolytic media hinder the industrial use

[5,6]. Solid catalysts can solve the problem of post-separation after hydrolysis, which show the advantage over liquid acid in recyclability [7-9]. In recent years, various kinds of heterogenous catalysts, including sulfonated carbons, sulfonated silica, zeolites have been reported in recent research [10-13]. Among them, sulfonated carbon catalysts have attracted much interest due to its low cost, hydrothermally stable, and high-performance characteristic [14-16]. Generally, the sulfonated carbon catalysts should be equipped with functional groups of sulfonic acid groups ( $-\text{SO}_3\text{H}$ ) and carboxyl group( $-\text{COOH}$ ) and hydroxyl group( $-\text{OH}$ ) anchored on the surface by the sulfonation treatment [17]. However, the common methods to prepare sulfonated carbon catalysts require hazardous chemicals, such as concentrated sulfuric acid (95%-99), chlorosulfonic acid, and fuming sulfuric acid ( $\text{SO}_3$  15%), higher reaction temperature and long reaction time [18-21]. So, there are still possible safety hazards and corrosion problems of reaction reactor. In attempts to improve catalytic performance, the

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pre-treatment of microcrystalline cellulose is also required. The strong oxidizing concentrated sulfuric acid and high sulfonated temperature contribute to the unstable carbon species, which will accelerate the deactivation of sulfonated carbon catalysts [22].

Li et al. firstly proposed a solution plasma sulfonation system by using dilute sulfuric acid [23]. But the solution plasma discharge only occurs inside a liquid, this plasma process is only applicable to hydrophilic carbon material [24]. In this work, gas-liquid interfacial plasma (GLIP) can overcome the shortcoming of solution plasma sulfonation, the plasma is generated on the interface between gas phase and liquid phase, which could be applicable to hydrophobic and hydrophilic carbon materials with different chemical and physical properties. Thus, we investigated the GLIP sulfonation performance on CNT in dilute sulfuric acid of 0.5 M to 2 M with the reaction time in the range of 15 min to 45 min. The GLIP sulfonated CNT has been applied to hydrolysis of cellulose to glucose. The influence of hydrolysis temperature and hydrolysis time have also been discussed for the conversion result and products distribution.

## 2. Experimental

### 2.1 GLIP sulfonation process

As shown in Fig. 1. The GLIP equipment was

composed of three main parts, including the power supply, vacuum pump, and main reaction chamber. Inside the chamber, hollow stainless-steel tubes were used as electrodes above the liquid phase. The distance between the tips of electrodes and liquid surface was controlled to 5 mm. Ar gas injection through the hollow stainless-steel tube electrodes assist the discharge of plasma on the interface between gas and liquid. The flow rate of Ar is about 1 sccm ( $\text{cm}^3/\text{min}$ ). The liquid used in GLIP sulfonation was 0.5 M to 2 M. A vacuum pump was used to keep the vacuum state during the entire discharge process. A high-voltage bipolar pulse generator (Pekuris MPP-HV04) was used as the power supply. The voltage, frequency and pulse width were fixed on 1 kv, 50 KHz, and 0.4  $\mu\text{s}$ , respectively. 0.3 g of CNT were put in 100 ml  $\text{H}_2\text{SO}_4$  and then transferred to the GLIP reactor. After plasma discharge treatment, the resulting solution were filtered and washed with DI water until the filter solution to be neutral, then the sulfonated CNT was drying in the oven at 80  $^\circ\text{C}$  for 12 h.

### 2.2 Hydrolysis of cellulose

A typical hydrolysis process was as follows: the mixture of 0.15 g microcrystalline cellulose and 0.135 g sulfonated carbon catalyst were mixed in 13.5 ml of DI water. Then transfer the solution to a 100 ml of Teflon-lined autoclave and followed by heating at 150

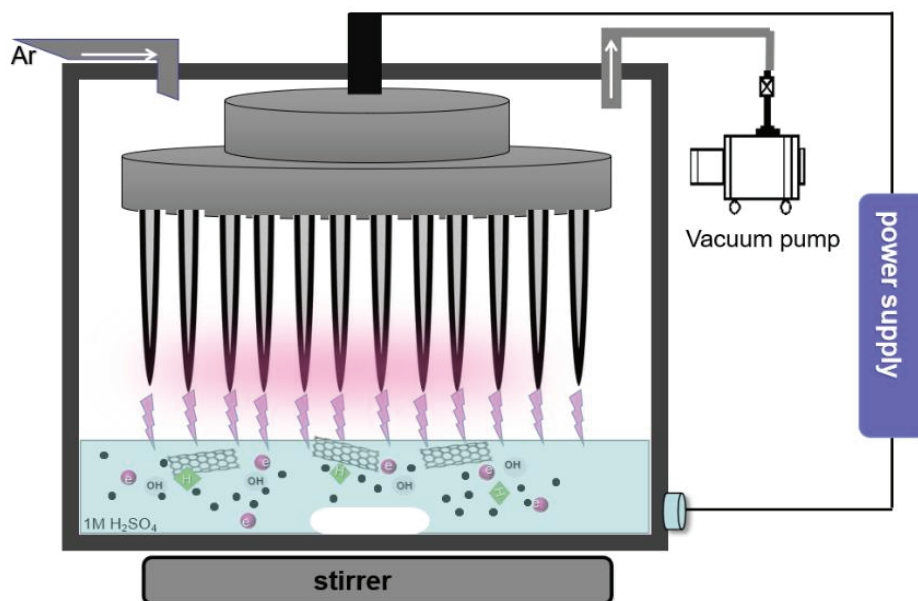


Fig. 1. Schematic of gas-liquid interfacial plasma reactor.

°C for 12, 15, 18 hours, respectively. Afterwards, the reducing sugars distribution after hydrolysis reaction were examined by high performance liquid chromatography (Shimadzu LC solution), which is equipped with Rezex roa-organic acid h+ column. The residual was filtered and washed with DI water adequately, then drying it in the oven with heating at 80 °C for 12 hours for the reuse examination.

### 3. Results and discussion

#### 3.1 Morphology and structure property

The morphology of CNT before and after sulfonation by GLIP can be observed in Fig. 2 (a) and (b). There is no significant difference between original CNT and sulfonated CNT. The arrangement of carbon nanotubes is not as dense as that original CNT. There is slight detraction of carbon structure after GLIP sulfonation. Fig. 3 illustrates the X-ray diffraction

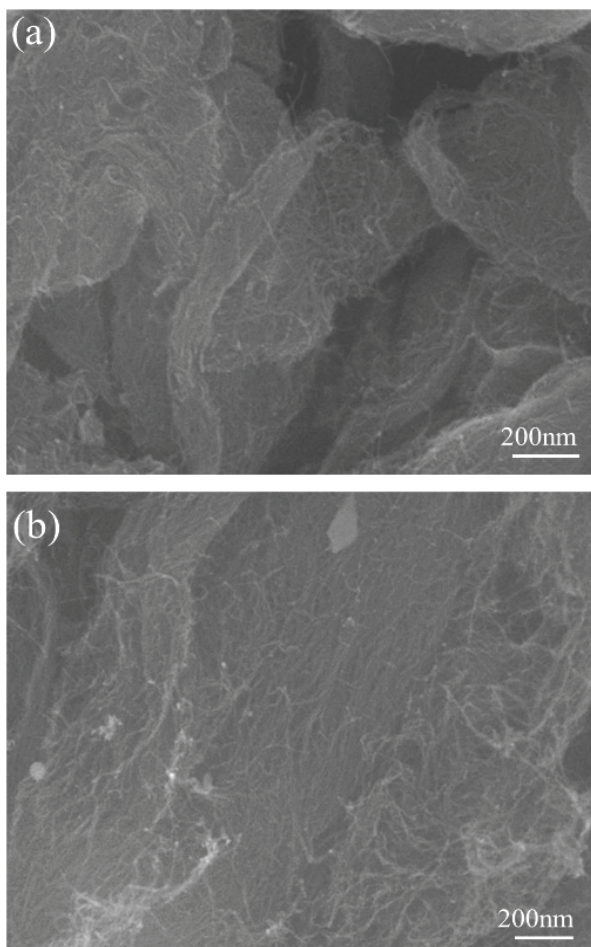


Fig. 2. SEM images of CNT before and after sulfonation in 2M H<sub>2</sub>SO<sub>4</sub> for 45min.

(XRD) patterns of CNT before and after sulfonation by GLIP. The broad diffraction peak ( $2\theta=20-25^\circ$ ) shows the characteristic of plane <002>, it is related to the amorphous carbon structure. The weak peak at around  $2\theta = 40-45^\circ$  is attributed to the axis of the graphite structure. No remarkable difference can be observed in the XRD patterns of carbons after sulfonation. It illustrates the limited structure damage on CNT after plasma treatment.

#### 3.2 Acid group density

The densities of -SO<sub>3</sub>H, -COOH and -OH, as well as total acid groups density of CNT after GLIP sulfonation under different concentrations of H<sub>2</sub>SO<sub>4</sub> were examined by using a typical acid-base titration method, as shown in Fig. 4. After sulfonation under 0.5M H<sub>2</sub>SO<sub>4</sub> for 15 min, the -SO<sub>3</sub>H density and total acid density of sulfonated CNT are 0.14 and 1.52 mmol/g. Under the condition of 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub>, the densities of -SO<sub>3</sub>H sites, -COOH and -OH sites can reach to 0.21 - 0.23 mmol/g and 1.66-1.93 mmol/g, respectively. The increasing of acid groups densities can be obtained after extending the processing time to 30 min, the sulfonic acid groups and total acid group under 0.5M, 1M, and 2M sulfuric acid can reach to 0.33 - 0.52, 2.03 - 3.08 mmol/g. With the reaction time rising to 45min, generally, there is a slight increase in acid groups density, the density of -SO<sub>3</sub>H, -COOH and -OH groups have been enhanced to 0.35 - 0.53 mmol/g and 2.63 - 3.64 mmol/g.

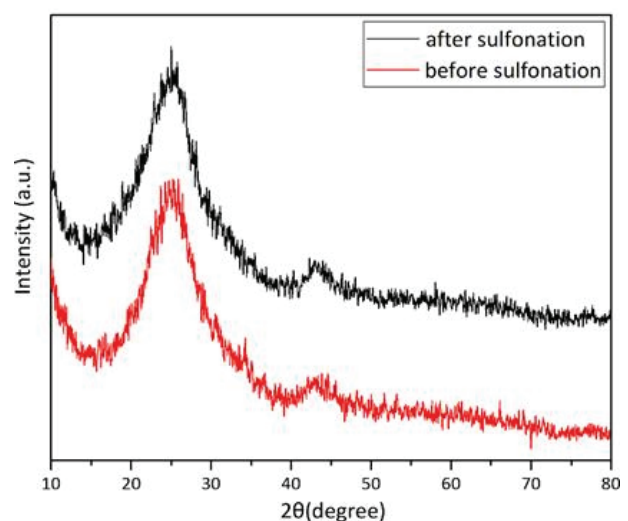


Fig. 3. XRD pattern of CNT before and after sulfonation by GLIP in 2M H<sub>2</sub>SO<sub>4</sub> for 45min.

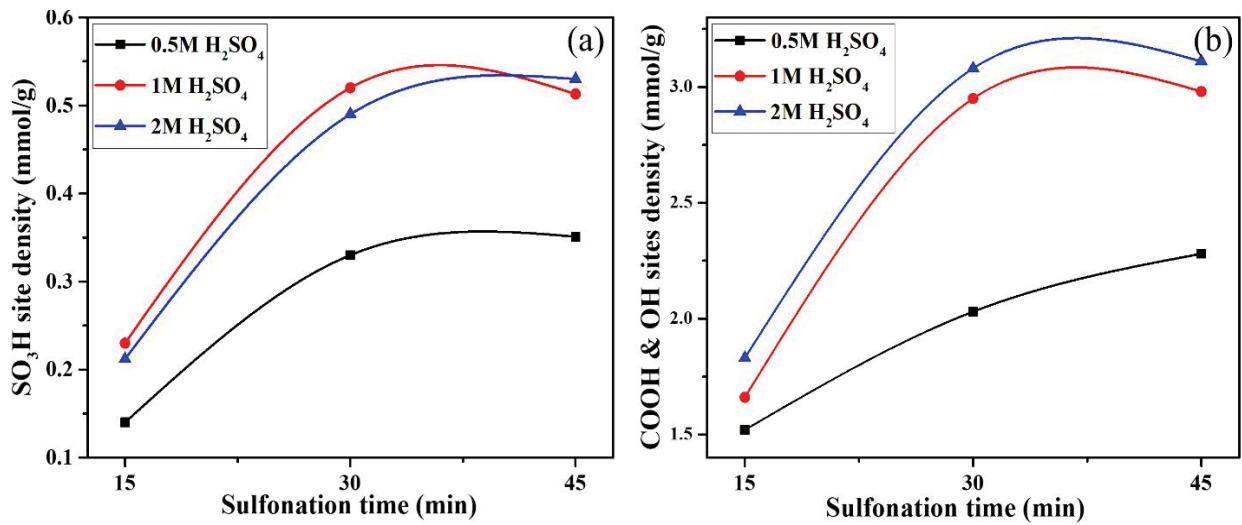


Fig. 4. SO<sub>3</sub>H site density (a) and COOH & OH sites densities (b) of GLIP sulfonated CNT prepared under 0.5M, 1M, 2M H<sub>2</sub>SO<sub>4</sub> for 15min, 30min, 45min, respectively.

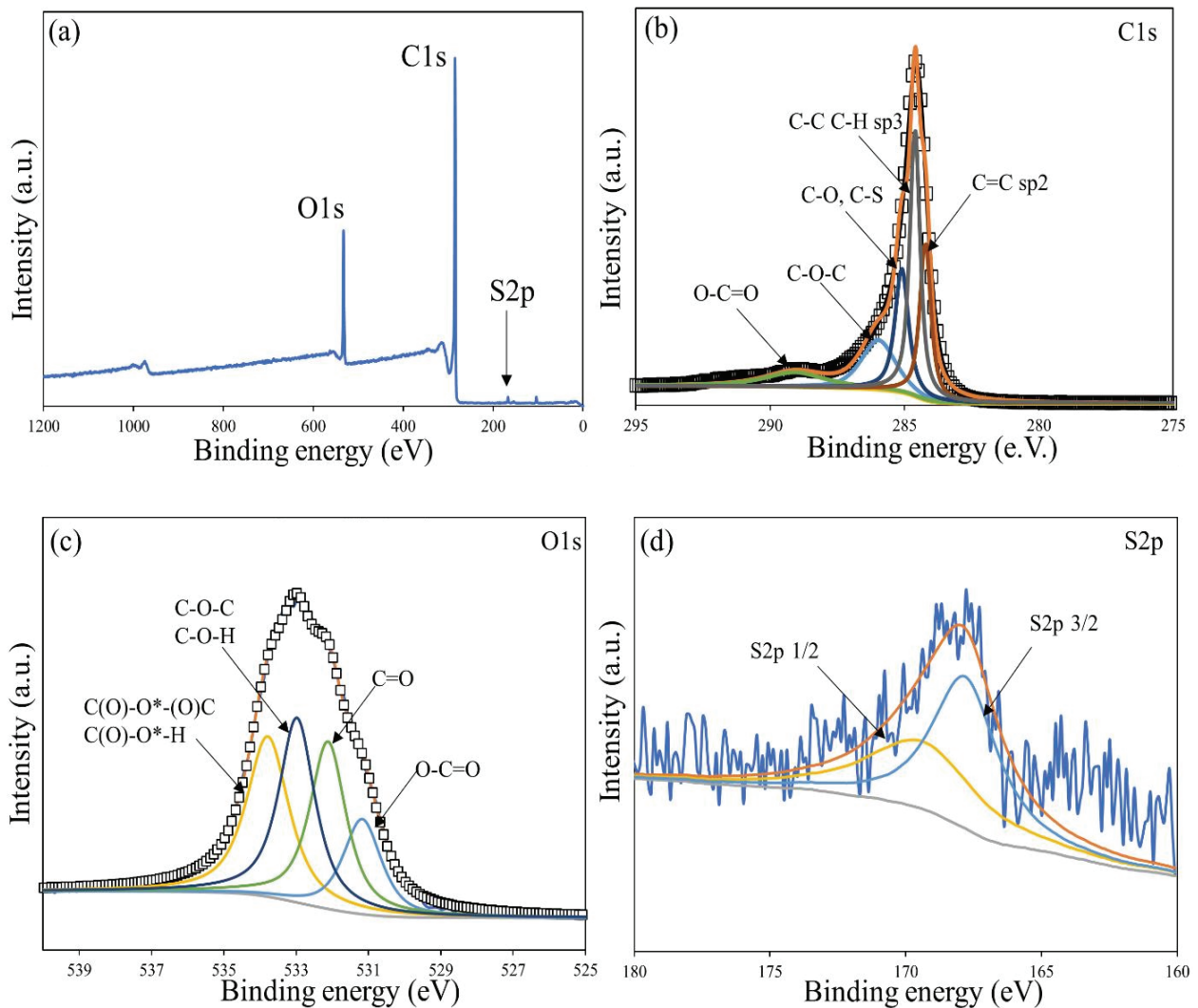


Fig. 5 XPS analysis of sulfonated CNT prepared by GLIP process. Sulfonation condition: 2M H<sub>2</sub>SO<sub>4</sub> Sulfonation time: 45min

### 3.3 XPS analysis

X-ray photoelectron spectroscopy (XPS) has been used to measure the elemental composition and chemical bonding distribution on the CNT after GLIP sulfonation. As shown in Fig. 5(a), the wide spectra includes the signal of C1s, O1s and S2p. XPS spectra of C1s can be divided into five peaks, 284.59 eV (C=C), 285.23 eV (C-C), 285.22 eV (C-O), 285.59 eV (C-O-C), 285.6 eV (O-C=O). The deconvoluted spectra of O1s can be assigned to the peak of O-C=O (531.22 eV), C=O (523.15eV), C-O-C, C-O-H (533.13 eV) and O=C-O\*-H (533.82eV), respectively. As shown in Fig. 5(c), the S2p deconvolution can be assigned to  $S2p^{1/2}$  at 169.55 eV and  $S2p^{3/2}$  at 168.35 eV, which confirms the presence of sulfonic acid groups on the carbon. Therefore, the GLIP process is efficiently to graft acid groups of -OH, -COOH, and  $SO_3H$  on the carbon.

### 3.4 Catalysis performance

As shown in Fig. 6, the catalytic performance of CNT sulfonated by GLIP process under 0.5 M, 1 M, 2 M  $H_2SO_4$  were demonstrated. The hydrolysis of microcrystalline cellulose (Alfa Aesar) was based on hydrothermal method under 150 °C for 12 h, 15 h, 18 h, respectively. The result shows that the main product is glucose, the side-products contain xylose, acetic acid, formic acid, and glycerol. For hydrolysis time of

12h, the glucose yield and total conversion rate prepared under 0.5 M - 2 M  $H_2SO_4$  are between 4.90 % - 8.91 %, 6.29 % -11.11 %. As the hydrolysis time increases from 12h to 15h, the glucose yield and total conversion rate have been enhanced to 6.94 - 10.15 % and 6.95 % - 13.37 %. The glucose yield and total conversion rate up to 7.23 % - 9.65 % and 10.39 - 16.83 % after 18 h of hydrolysis. The sulfonated CNT prepared under 1 M and 2 M of sulfuric acid provides higher hydrolysis activity than the catalysts prepared under 0.5 M  $H_2SO_4$ , where the glucose yield and conversion rate can achieve 12.95 % - 13.32 %, 16.73 % - 17.83 % after 18 h of hydrolysis reaction, respectively. It agrees with the acid groups doping result measured by titration method.

The hydrolysis temperature is one of essential factor for the hydrolysis performance. Fig. 7 illustrates the temperature influence on cellulose conversion, hydrolysis temperature of 120 °C, 150 °C and 180 °C have been applied to hydrolysis of cellulose for 18h. Under the hydrolysis temperature of 12 h, the total conversion rate dropped by 53.23 %, from 16.83 % to 7.87 % compared to 15 h hydrolysis. The selectivity of glucose was 83.46 %, which was higher than that under 150 °C of 79.16 %. High hydrolysis temperature plays positive effect on the catalytic activity of sulfonated CNT. The total conversion rate increased from 16.83 % to 19.39 % after rising the temperature

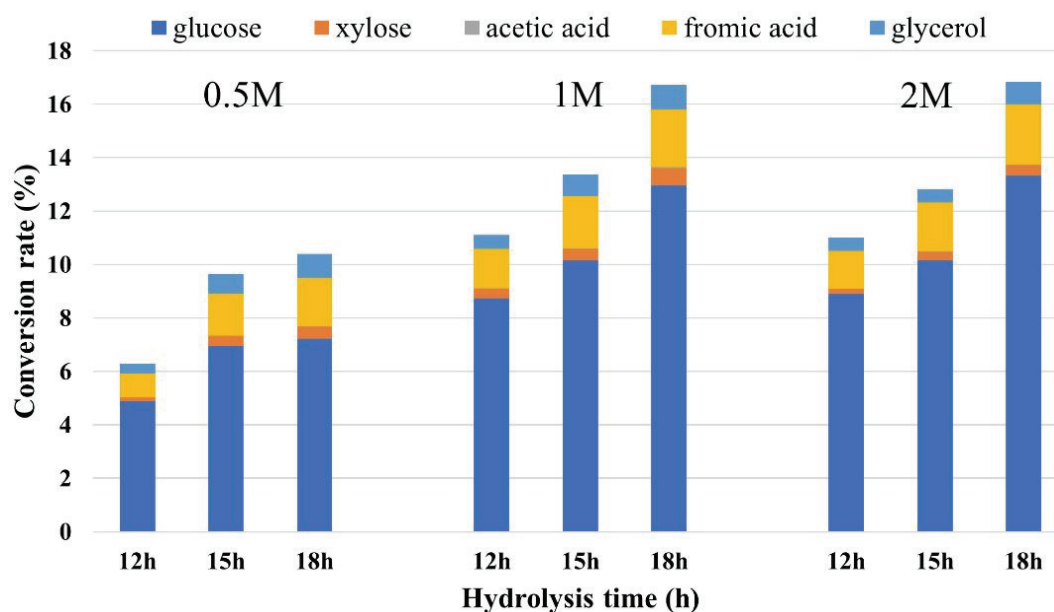


Fig. 6. Hydrolysis result by using sulfonated CNT. Sulfonation time: 45min; Hydrolysis temperature: 150°C.

to 180 °C.

As exhibits in Fig. 8, the recycle ability of GLIP sulfonated CNT was characterized by reuse experimental for cellulose hydrolysis under identical hydrothermal condition. The first use of sulfonated

CNT results in glucose yield, conversion rate and glucose selectivity of 14.79 %, 18.43 % and 80.23 %. The glucose yield and conversion rate after first recycle were about 13.67 % and 17.37 %, the decrease of glucose yield and conversion rate were

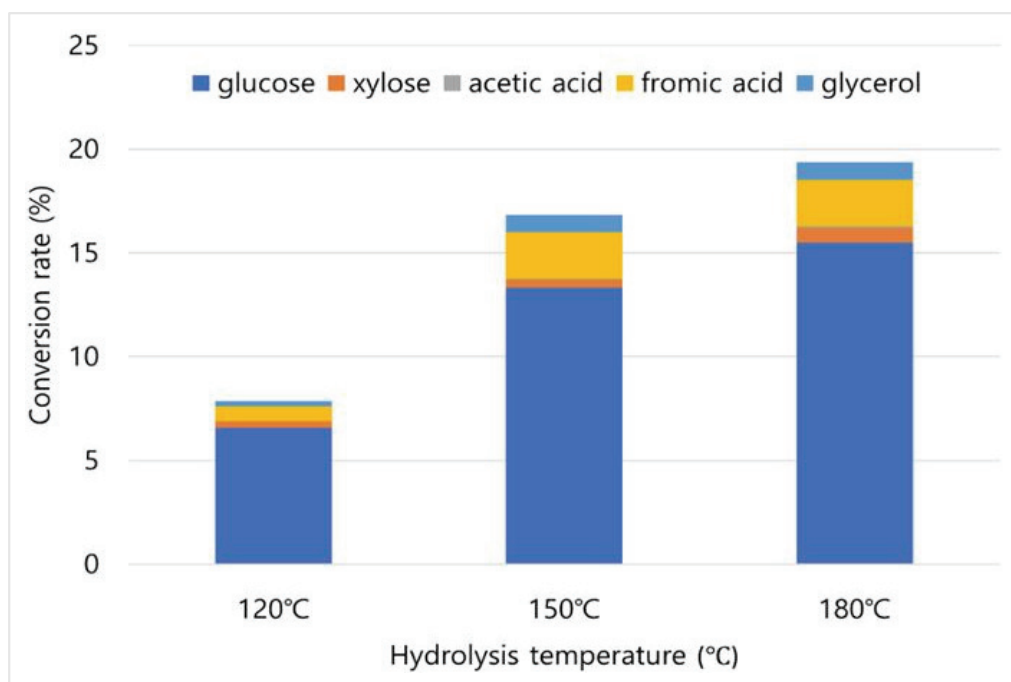


Fig. 7. Temperature effect for the hydrolysis result by using sulfonated CNT. Sulfonation condition: 2M sulfuric acid; Sulfonation time: 45min; Hydrolysis condition: Cellulose: 0.135g; Catalysts: 0.15g Water: 13.5ml; Hydrolysis time: 18h.

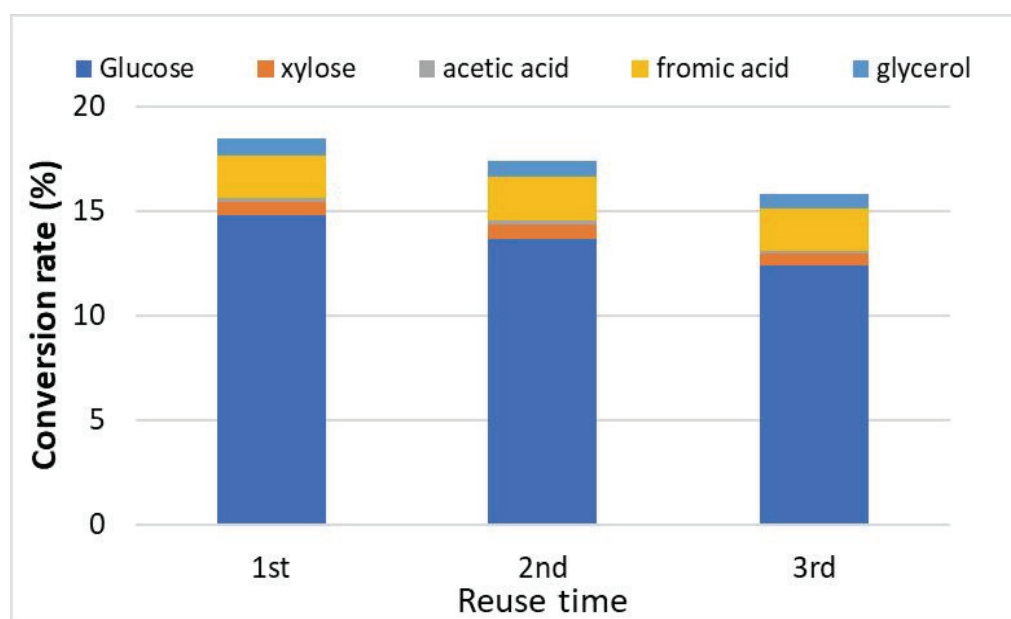


Fig. 8. Reuse test of sulfonated CNT for hydrolysis of cellulose. Sulfonation condition: 2M sulfuric acid; Sulfonation time: 45min; Hydrolysis condition: Cellulose: 0.135g; Catalysts: 0.15g Water: 13.5ml; Hydrolysis time: 18h.

1.12 % and 1.06 %. There was slight reduction of hydrolysis activity after the third time use of the sulfonated CNT catalysts, the glucose yield and total conversion rate reduced to 12.38 % and 15.80 %. The exfoliation of carbon species that doped with functional acid sites lead to the deactivation of the sulfonated CNT catalysts during recycling process. However, compared with hydrothermal sulfonation conduction in concentrated H<sub>2</sub>SO<sub>4</sub> under high temperature, the structure damage caused by the GLIP sulfonation is relatively weak, the activity of the catalytic carbon species is much stable. Therefore, it benefits that the catalytic ability can maintain 85.73 % after three times use, which is comparable to the sulfonated carbon catalysts reported in literature. [25,26].

#### 4. Conclusions

In conclusion, sulfonated carbon catalysts were successfully synthesized via GLIP under dilute sulfuric acid at room temperature. The influence of sulfuric acid concentration has been discussed by using gradient concentration (0.5 M, 1 M and 2 M) of H<sub>2</sub>SO<sub>4</sub>. After GLIP sulfonation, the -SO<sub>3</sub>H and total acidic densities can reach 0.53 mmol/g and 3.64 mmol/g, under 2 M H<sub>2</sub>SO<sub>4</sub> sulfonation for 45 min, respectively. 2 M H<sub>2</sub>SO<sub>4</sub> enable higher amount of functional acid groups doped on the carbon than 0.5 M / 1 M H<sub>2</sub>SO<sub>4</sub>. The GLIP sulfonated CNT has been applied to conversion of cellulose to glucose. The effect of hydrolysis temperature (120 °C, 150 °C, 180 °C) and time (12 h, 15 h, 18 h) have also been investigated. The maximum total conversion rate of 19.39% can be obtained under 180 °C for 18 h. The recyclability of sulfonated CNT under the hydrolysis condition of 180 °C for 18 h can maintain 85.73 % after three times reuse, which verifies the excellent hydrothermal stability of sulfonated CNT catalysts by using GLIP sulfonation approach. GLIP sulfonation system is superior to traditional surface modification method in terms of H<sub>2</sub>SO<sub>4</sub> concentration, reaction temperature and reaction time. Gas-liquid interfacial plasma is a novel and soft surface way to modify carbon materials with functional acid groups for the application on biomass conversion.

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