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Preparation of polypropylene based hyperbranched absorbent fibers and the study of their adsorption of CO_2

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Abstract: Ring-opening copolymerization of aziridine in situ into substrates for introducing polyethyleneimine (PEI) not only required strict experimental condition but employed highly toxic monomer aziridine. In this paper, an effective and safe new procedure is developed for hyperbranched structure synthesis by stepwise growth using N-(2-Chloroethyl)-Benzaldimine as a monomer. A hyperbranched solid amine fibers for CO_2 capture were prepared through co-irradiation grafting copolymerization of Polypropylene fiber with glycidyl methacrylate, followed by amination with ethylenediamine, hoffman alkylation with N-(2-Chloroethyl)-Benzaldimine and then hydrolysis to remove benzaldehyde group. It was shown that the adsorption performance of the hyperbranched solid amine fibers G2.0 and G3.0 has greatly been improved compared with the first generation G1.0 fiber, and the adsorption capacity of G2.0 and G3.0 were 5.35 mmol/g and 5.53 mmol/g at 30 ^{o}C, respectively. The amine utilization of G2.0 fibers could reach 84.1%. These results demonstrated that the branched structure could promote the adsorption capacity and efficiency greatly due to its low mass transfer resistance of CO_2, more favorable than linear amination reagent.

Key words: CO_2 adsorption, polypropylene, hyperbranched, N-(2-Chloroethyl)-Benzaldimine

1. Introduction

Global warming is mainly attributed to an increase in atmospheric levels of CO_2 which is attributed to the tremendously promoted burning of fossil fuels[1]. The most effective method to reduce CO_2 emission is scrubbing the flue gas stream with an amine solution. But it brings some disadvantages such as corrosion, high regeneration energy and solvent degradation[2, 3]. To solve these problems, solid amine adsorbents such as amine-treated MCM-41[4, 5], SBA-15[6, 7], Zeolite 13X[8, 9] and activated carbon[10, 11] have been used, attracting much attention. The solid amine adsorbents can keep high adsorption capacities even in the presence of water, compared with those microporous or mesoporous adsorbents without amine modified. What's more, they can also be regenerated in mild conditions. The adsorption capacity of CO_2 mainly depends on the amine loading and the pore volume of the porous substrates. However, increasing amine loading will block the pore volume of the porous substrate, thus reducing the adsorption capacity of CO_2[6, 12]. So it has great significant to develop alternative substrate or improve amine agents to increase amine loading without affecting adsorption performance.

Much work advocating the usage of the fibrous adsorbent for CO_2 adsorption has been published by our group[13-16], demonstrating the fiber as a great potential substrate in CO_2 adsorption. The fibrous adsorbent possesses advantages of large external surface area, short transit distance, low pressure drops, and flexibility. Yang[15] grafted allylamine onto polyacrylonitrile fiber and obtained the adsorption ability of 6.22 mmol/g PAN-AF when the grafting degree came to 60.0 wt%. Zhuang[16] grafted glycidyl methacrylate onto polypropylene fibers, followed by reacting with triethylenetetramine to make a novel kind of solid amine-containing fibrous adsorbent and obtained the adsorption ability of 4.72 mmol/g. What's more, the adsorbent could maintain almost constant adsorption behavior within six recycles.

In 1990, Kim put forward the concept of "hyperbranch", then it became one of the most hot research topics of Polymer Chemistry[17]. Unlike dendritic molecular, hyperbranched moleculars did not require uniform structure and high symmetry, thus it was easy for preparation. The most important thing was that hyperbranched moleculars have lots of functional group that could both improve the hydrophilicity of material and increase the adsorption sites as an adsorbent[18, 19]. Among them, polyethyleneimine (PEI) for its high amine content and hyperbranched structure was widely reported to modify silicon dioxide[20, 21] and fibers[13, 14] that used for gas separation. The in situ ring-opening polymerization of aziridine into porous silica for introducing PEI to synthetize hyperbranched polymers has been conventionally carried out and used for CO_2 capture. However, on one hand, the approach has some additional disadvantages such as the usage of highly toxic monomer aziridine and strict experimental condition[22, 23]. On the other hand, Li[24] has studied the effect of molecular weight of PEI on the CO_2 capture performance of PEI-nano silica adsorbents and found that PEI with high molecular weight would lead an unsatisfactory amine utilization for its high steric hindrance due to the increased viscosity. Thus the development of PEI with low molecular weight and with an accessible structure will be benefit to improve its adsorption capacity and the amine efficiency.

In the study, an effective and safe new procedure is developed for hyperbranched structure synthesis by stepwise growth using N-(2-Chloroethyl)-Benzaldimine as a monomer. The hyperbranched solid amine fibers for CO_2 capture were prepared through co-irradiation grafting copolymerization, followed by amination, hoffman alkylation and hydrolysis. The effects of the branched structure on the adsorption performance of the fiber have been investigated.

2. Experimental

2.1 Materials and Reagents

Glycidyl methacrylate (GMA, Sigma-Aldrich CO) was used after the removal of the inhibitor with neutral aluminum oxide. Polypropylene (PP) fibers were provided by Xinshun Special Fiber Company (Zhongshan, China). Methanol, ethanol, triethylamine (TEA), hydrochloric (HCl), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), magnesium sulfate anhydrous ($MgSO_4$), benzaldehyde, ammonium ferrous sulfate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$), sodium hydroxide (NaOH), potassium iodide (KI) and ethylenediamine (EDA) were all purchased from Guangzhou chemical Reagents Factory. Diethylenetriamine (DETA) was purchased from Tianjin Fuchen chemical Reagents Factory. 2-chloroethylamine hydrochloride was purchased from Aladdin. Ether was provided by Kaixin chemical industry co. (Hengyang city). All reagents above were analytical grade (AR).

2.2 Preparation of hyperbranched solid amine fibers

2.2.1 Synthesis of N-(2-Chloroethyl)-Benzaldimine (CEBI)[25]

To a 250 mL three-neck round bottom flask was added 5.3 g (50 mmol) benzaldehyde, 5.8 g (50 mmol) 2-chloroethylamine hydrochloride, 10 g $MgSO_4$ and 50 mL anhydrous ether. Then a mixed solution (5.6 g (55 mmol) TEA and 50 mL anhydrous ether) was added to the reaction system in drops in 30 min. The reaction was carried out at room temperature, and stirred for 6 hours. After reaction, the solvent was removed in vacuo to obtain N- (2 - Chloroethyl) – Benzaldimine (CEBI).

2.2.2 Synthesis of PP-GMA

PP, GMA and DMF were added into a 250 mL conical flask, and then subjected to γ-ray irradiation. After irradiation, the grafted fiber (PP-GMA) was washed with DMF, and then dried at 60 ^{o}C for 12 h. The grafting degree of PP-GMA was calculated using equation (1):

$$G_{GMA} = \frac{W_1 - W_0}{W_0} \times 100\% \qquad (1)$$

Where W_0 and W_1 are the weights (g) of the original and grafted PP fiber, respectively.

2.2.3 Synthesis of G1.0 fiber PP-GMA-EDA

PP-GMA, $AlCl_3$•$6H_2O$ and EDA were mixed and added into 100mL three neck flask. The reaction was carried out at 105 ^{o}C for 6 h. After reaction, the product Fiber (G1.0, PP-GMA-EDA) were washed with deionized water thoroughly to remove the residual $AlCl_3$ and EDA, then dried at 60 ^{o}C for 12 h. Contents of primary or secondary amines (N, mmol/g) of G1.0 fibers was calculated by the following equation:

$$n(\text{Primary Amine}) = n(\text{Secondary Amine}) = \frac{1}{2} \times n(\text{Amine}) = \frac{1}{2} \times \frac{E}{14} \times 1000 \qquad (2)$$

Where E was mass fraction of nitrogen measured by elemental analysis.

2.2.4 Synthesis of G1.5 fibers by hoffman alkylation PP-GMA-EDA-CEBI

1.5 g PP-GMA-EDA (G1.0) Fiber, 60mL deionized water and 1.32 g KI were added into a 100 mL three-neck flask, then a certain amount of CEBI in 30 mL Anhydrous methanol were slowly dropped into the reaction system. After reflux of the solution at 60 ^{o}C for 12 h. the obtained fiber (G1.5, PP-GMA-EDA-CEBI) was washed with excess deionized water and anhydrous ethanol, and then dried at 60 ^{o}C for 12 h.

2.2.5 Synthesis of G2.0 fibers PP-GMA-EDA-CEA

The bulky phenyl groups of CEBI was removed from G1.5 fiber by mixing the PP-GMA-EDA-CEBI G1.5 Fiber with 4M HCl (90 mL) and reacted at 30 ^{o}C for 8 h. Then the fiber was washed with 1M NaOH and with deionized water until the solution turned neutral. And the resulting product G2.0 fiber (PP-GMA-EDA-CEA) was dried at 60 ^{o}C under vacuum. The contents of primary, secondary, tertiary amines or imine (N, mmol/g) of G2.0 fibers were calculated by the following equation:

$$\mathrm{n(iAmine)}=\frac{\mathrm{A_i}}{\sum \mathrm{A_i}}\times\frac{\mathrm{E}}{14}\times 1000 \tag{3}$$

i= Primary, Secondary, Tertiary and Imine

Where E was mass fraction of nitrogen measured by elemental analysis. A_i represented different types of nitrogen's peak area tested by X-ray photoelectron spectrometer.

2.2.6 Synthesis of G2.5 and G3.0 fibers

The experimental conditions used to prepare G2.5 and G3.0 fibers were the same as the description of G1.5 and G2.0 fibers, and the calculation method of different types of amine could refer to equation (3).

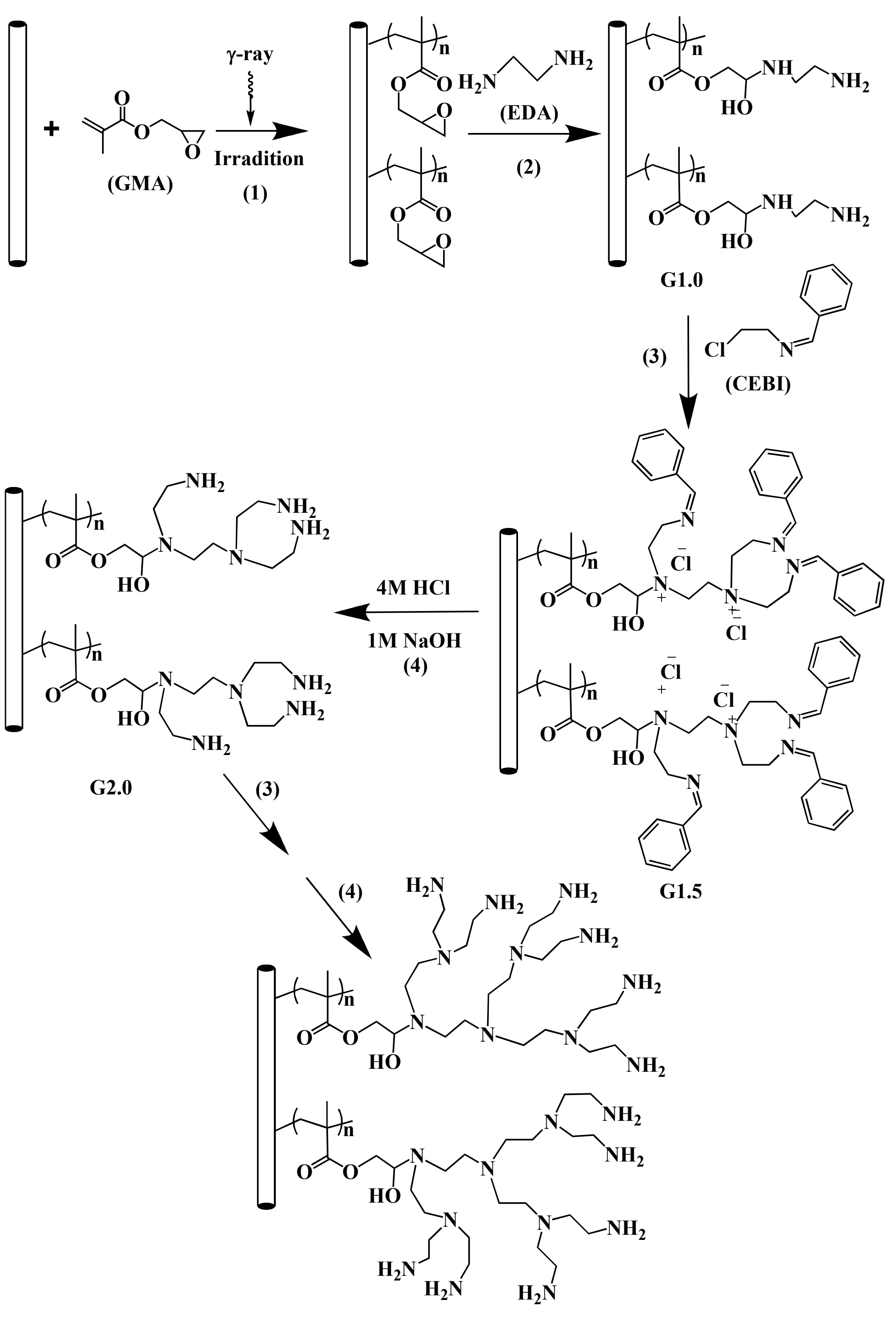
The preparation scheme of the hyperbranched solid amine fibers was presented in Scheme 1.

2.2.7 Synthesis of G1.0-DETA fibers

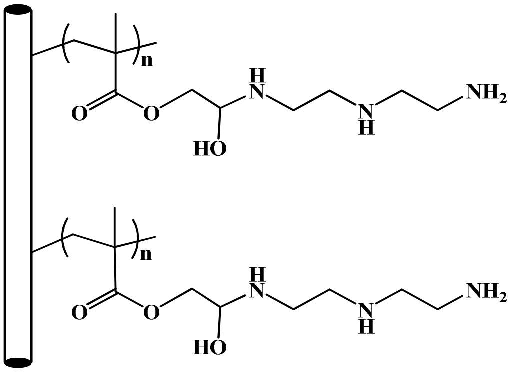
In order to evaluate the effect of the structure of amination reagent on the adsorption, G1.0-DETA fibers (PP-GMA-DETA) were synthesized through using DETA, instead of

EDA, to react with G0.5 PP-GMA fibers. DETA was an amination reagent with a longer linear chain. The experimental conditions used to prepare G1.0-DETA fibers were referred to the description of G1.0 fibers. The structure of G1.0-DETA fiber was presented in Scheme 2.

In general description, all modified fibers of G1.0, G2.0 and G3.0 with amino groups as end groups are described as full generation fibers; and those fibers of G0.5, G1.5, and G2.5 with phenyl groups as the end groups are described as half generation fibers.



Scheme 1. Reaction scheme of hyperbranched adsorbent fibers preparation



Scheme 2. Structure of G1.0-DETA fiber

2.3 Physical and Chemical Characterization

Infrared (IR) spectra (Tensor-27 spectrometer), Elemental analysis (Elementar, Vario EL), solid state ^{13}C NMR analysis (AVANCE AV, Bruker) and X-ray photoelectron spectroscopy (ESCALAB 250, Thermo-VG Scientific) were used to confirm the structure of the polymers.

Thermo gravimetric analyzer (Netzsch TG-209) was employed to determine the thermal stability of different full generation samples. The test was carried out from 100 ^{o}C to 600 ^{o}C by a heating rate of 10 K/min.

2.4 CO_2 Adsorption Experiment

1.0 g fiber samples were placed into a specially designed glass tube (Φ=13 mm), followed by purging dry N_2 to remove air and excess water. Then a mixture gas (CO_2 : N_2 = 1:9 (volume ratio)) whose flow rate was 30 mL/min was introduced. The outlet CO_2 concentration was determined by the gas chromatography (Techcomp 7900) with a thermal-conductivity detector.

The adsorption amount was calculated as follows:

$$Q = \int_0^t \left(C_{im} - C_{eff}\right) V\ dt/22.4W \qquad (4)$$

Where Q represented the adsorption capacity (mmol CO_2/g), t was the adsorption time (min). C_{im} and C_{eff} were the influent and effluent concentrations of CO_2 (vol%), respectively. V was the total flow rate, 30 mL/min; W and 22.4 were the weight of sample (g) and molar volume of gas (mL/mmol), respectively.

After adsorption, the fiber was regenerated by purging N_2 with a flow rate of 30 mL/min at 90 ^{o}C.

3. Result and discussion

3.1 Chemical characterization

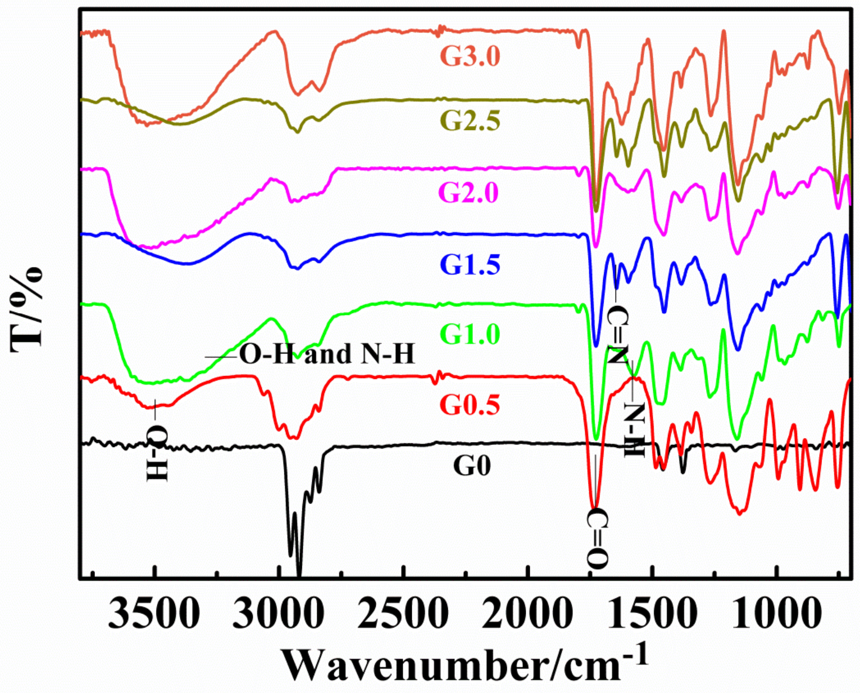


Fig 1. FT-IR spectra of G0, G0.5, G1.0, G1.5, G2.0, G2.5, G3.0 fibers

Fig 1 shows the FT-IR spectrum of grafted fibers at each stage. Compared with G0 fibers, there is a sharp band at 1736 cm^{-1}, which is attributed to C=O stretching vibration of grafted GMA. In addition, a broad and strong absorption band at 3412 cm^{-1} is attributed to O-H bending vibration. The intensity of this band at 3412 cm^{-1} increased after amination because it was the overlap of O-H and N-H bending vibration. The result above proved EDA was successfully introduced onto the surface of the material. And it is found that there was only a band at 1542 cm^{-1} for N-H in-plane bending vibration in the range from 1550 cm^{-1} to 1650 cm^{-1} for the full generation fiber (G1.0, G2.0 and G3.0), but there was another band at 1640 cm^{-1} for C=N stretching vibration for the half generation (G0.5, G1.5 and G2.5), demonstrating the successful preparation of hyperbranched absorbent.

Tab 1. Element analysis of G0, G0.5, G1.0, G2.0 and G3.0 fibers

Fibers	WG[a] (g / g raw material)	Element content (wt%)			Amine content (mmol/g)
		C / %	H / %	N / %	
G0	—	84.30	13.66	0.00	—
G0.5	3.12	65.59	9.02	0.00	—
G1.0	0.25	50.88	9.46	8.46	6.04
G2.0	0.30[b]	53.57	9.42	10.86	7.76
G3.0	0.22[c]	52.74	9.34	12.09	8.64

[a] $WG = \frac{W_p - W_r}{W_r}$, Where WG represented the weight gain (g / g raw material), W_r and W_p were the weight of the raw material and product, respectively. [b] The unknown quantities of Cl^- would affect the calculation if the raw material referred to G1.5. Thus for the accuracy and convenience, the raw material in this step referred to G1.0. [c] The raw material in this step referred to G2.0.

Tab 2. The amine type and content of G1.0, G2.0 and G3.0 fibers

Fibers	Amine content(mmol/g)				
	total	primary	secondary	tertiary	imine
G1.0	6.04	3.02	3.02	—	—
G2.0	7.76	2.58	1.89	1.89	1.39
G3.0	8.64	2.84	2.29	2.02	1.48

In order to determine the type of the nitrogen and whether the structure was a linear chain or a branched one, element analysis, X-ray photoelectron spectroscopy and ^{13}C NMR spectra were carried out and presented in Tab 1, Tab 2, Fig 2 and Fig 3, respectively. Compared with G0, both the content of carbon and hydrogen of G0.5 decreased and the calculated grafting degree according to the element analysis was 326%, corresponding well to the result measured from weight gain (312%). After aminiation with EDA, the nitrogen content of G1.0 reached up to 6.04 mmol/g, similar to the data (6.67 mmol/g) calculated by weight gain. Furthermore, it was obvious that the nitrogen content of the full generation increased with the increasing of the generation, proving that the monomer (CEBI) was successfully introduced onto the surface of the fibers. However, the amine number of G2.0 and G3.0 from weight gain was a little lower than that from the element analysis, which could be attributed to the difficult collecting of G2.0 and G3.0 after treatment by strong acid and strong base that led to the brittleness of the fibers. Moreover, with respect of G2.0 and G3.0, the incomplete hydrolysis confirmed by the ^{13}C NMR spectra that the chemical shift of benzyl and imine groups appears at 130 ppm and 140 ppm respectively, gave the explanation for the lower amine content than expected. In addition, as shown in Tab 2, combining the element analysis data and X-ray photoelectron spectroscopy[26, 27], the number of different amines was calculated and listed in Tab 1. The presence of tertiary amine implicated that the branching can happen to form a hyperbranched polymer.

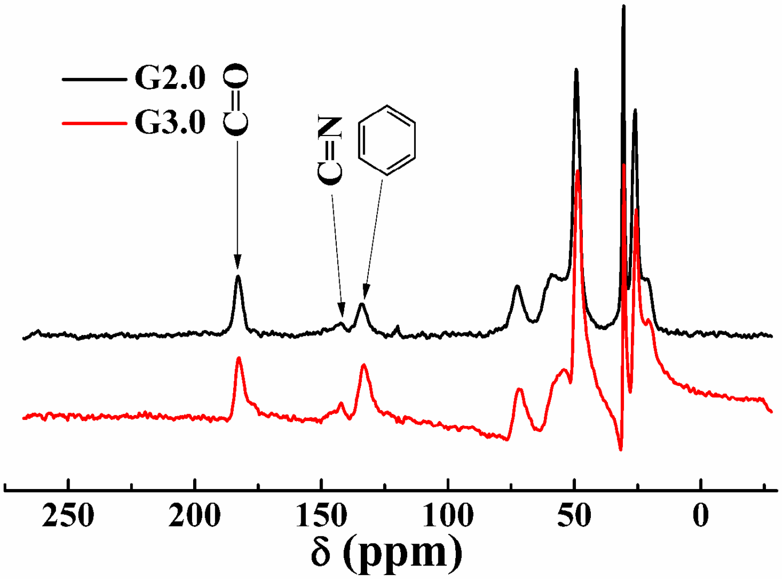


Fig 2. ^{13}C NMR spectra for G2.0 and G3.0

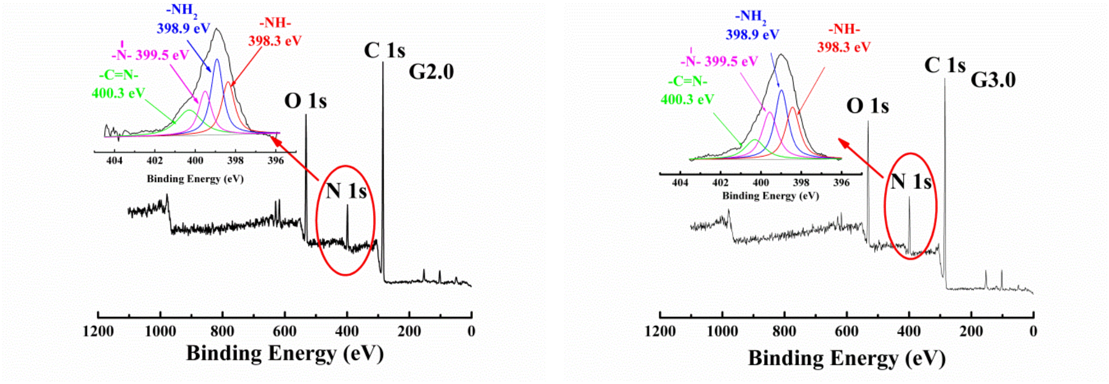


Fig 3. Typical XPS wide scan spectra for G2.0 and G3.0. The inset shows the characteristic peaks of N 1s with higher resolution

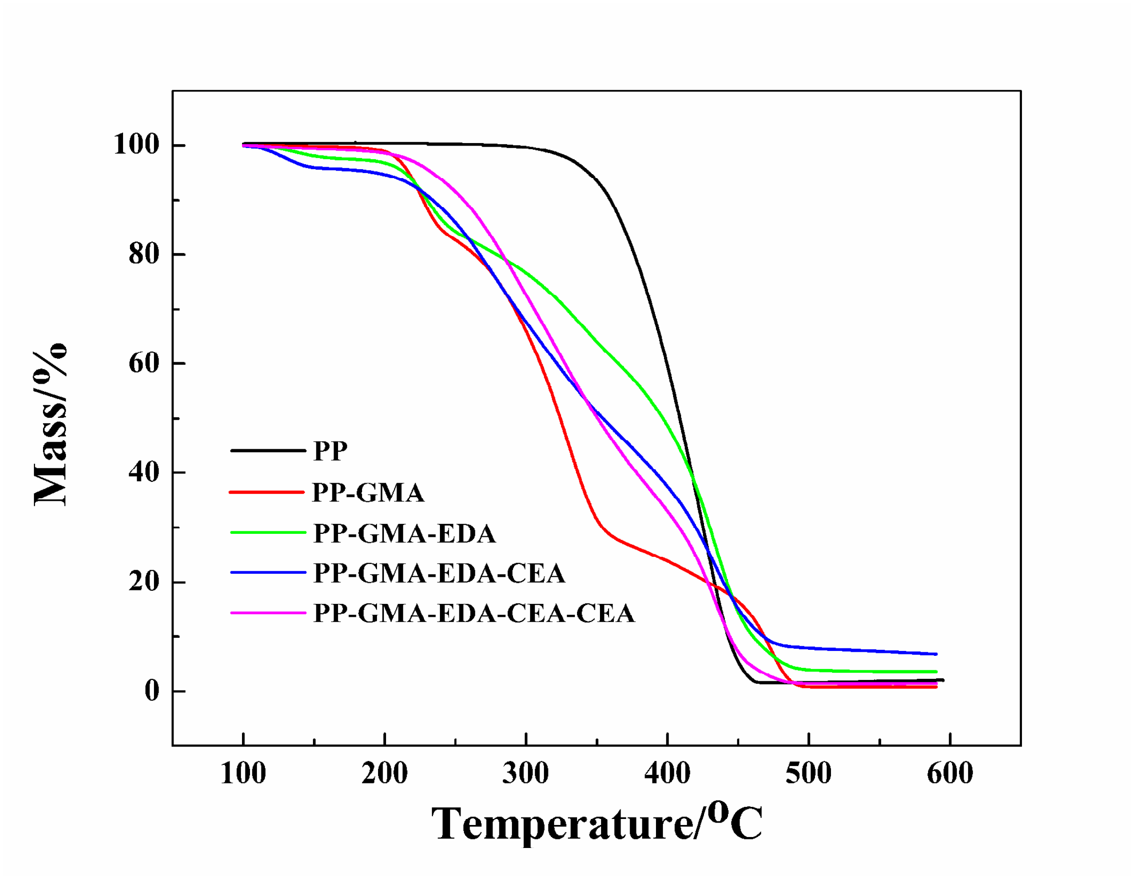


Fig 4. The thermo gravimetric curve of different generation absorbent fibers

Results of TG analysis of different generation absorbent fibers were presented in Fig 4. In the case of PP, there was only one continuous weight loss from 310 °C to 460 °C. In the TG curve of PP-GMA, three distinct weight loss steps were observed at 200 °C, 260 °C, and 350 °C. The first weight loss could be attributed to decomposition of the homopolymer, and the second one between 260 °C and 350 °C was probably related to the degradation of GMA, which also indicated that the monomer GMA was grafted onto the surface of PP. Comparing the G1.0, G2.0 and G3.0 fibers, the thermal stability was G3.0>G1.0>G2.0. As is known to all, increasing chain length would reduce the thermal stability. However, G3.0 with the longest chain length performed better stability than the first two generations, overcoming the defect.

3.2 Adsorption property

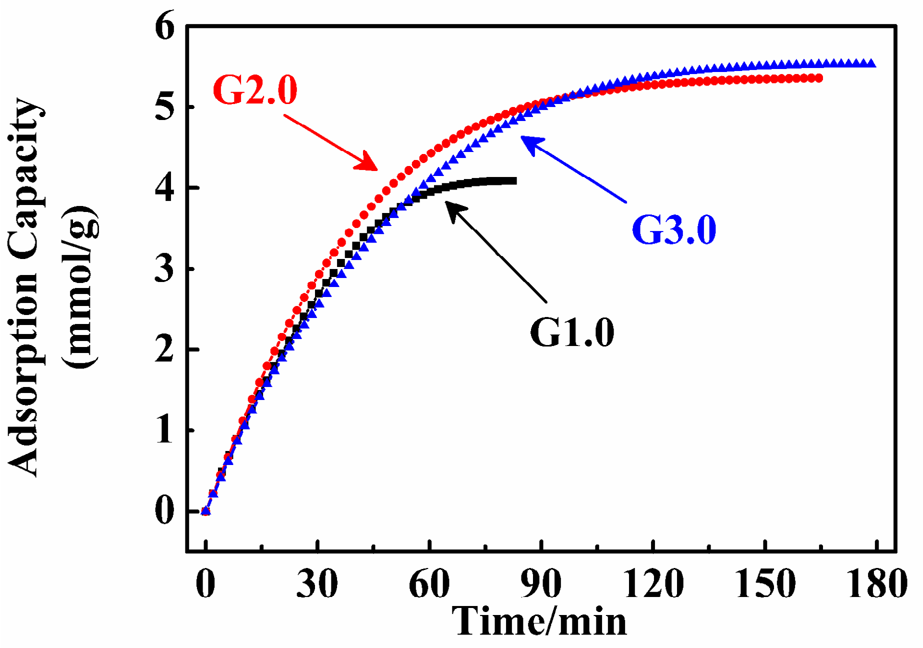


Fig 5. The cumulative adsorption curve of G1.0, G2.0, G3.0 fibers (adsorption temperature: 30 °C; N_2: 27mL/min; CO_2: 3 mL/min)

The cumulative adsorption curves were shown in Figure 5, and the adsorption capacity and amine utilization efficiency of G1.0, G2.0, G3.0 fibers were shown in Table 2. With the increase of fiber generation, the adsorption capacities increased due to the increase of alkyl amine content, demonstrating the importance of high amine content.

However, the equilibrium adsorption time increased for the thickening of the adsorption layer which would extended the diffusion time. Moreover, the efficiency of G3.0 decreased to 77.3% while the G2.0’s reached to 84.1%, which could be ascribed for the longer chain length that increased the steric resistance and disfavored the adsorption. It reminds us of a fact that an appropriate amination reagent which could combine alkyl amine content with lower steric resistance should be chosen.

Tab 3. The adsorption capacity and amine utilization efficiency for CO_2 of G1.0, G2.0, G3.0 and G1.0-DETA

(adsorption temperature: 30 ^{o}C; N_2: 27mL/min; CO_2: 3 mL/min)

Samples	Alkyl amine (mmol/g)	Adsorption capacity (mmol/g)	Efficiency(%)
G1.0	6.04	4.08	67.5
G2.0	6.36	5.35	84.1
G3.0	7.15	5.53	77.3
G1.0-DETA	6.64	3.59	54.1

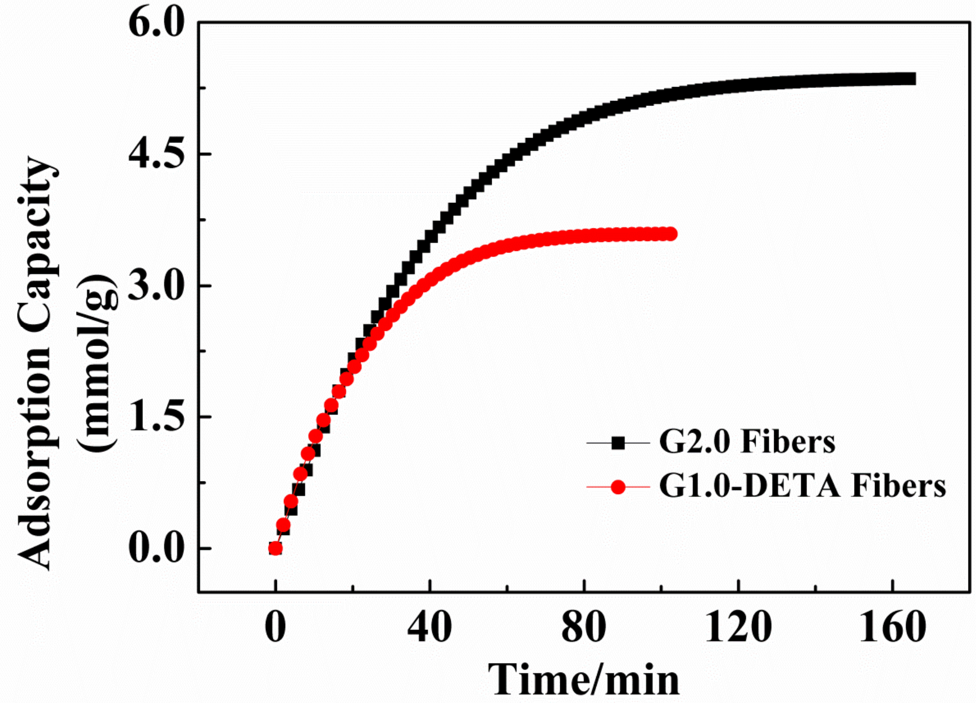


Fig 6. The cumulative adsorption curve of G2.0 and G1.0-DETA fibers (adsorption temperature: 30 °C; N_2: 27mL/min; CO_2: 3 mL/min)

For the purpose of studying the effect of branched structure on the CO_2 adsorption performance, DETA was employed and immobilized onto PP-GMA fiber. Since G2.0 (PP-GMA-EDA-EDA) and G1.0-DETA (PP-GMA-DETA) fibers had similar nitrogen content, the influence of amine content on the adsorption capacity was excluded based on the mechanism with the presence of water vapor[28, 29]. In addition, G2.0 (PP-GMA-EDA-EDA) had a branched structure, and G1.0-DETA (PP-GMA-DETA) had a linear one. The adsorption capacities and efficiency of G2.0 and G1.0-DETA were compared. As described in Figure 6 and Table 3, in the early stages, the adsorption rate of G1.0-DETA was almost the same (before 20min) as the G2.0's, and the adsorption capacities of two materials were 2 mmol/g at that stage. The results may attribute to the similar numbers of their primary amines on the outer layer. After 20min, the adsorption rate of G1.0-DETA became slow on account of the higher mass transfer resistance of CO_2 into the inner layer for the molecular chain entanglement. Meanwhile, the molecular chain entanglement would also prevent the adsorption sites from reacting with CO_2. Both the adsorption capacities and the amine utilization of G2.0 fiber were much higher than G1.0-DETA's. The above results demonstrated that the branched structure of G2.0 (PP-GMA-EDA-EDA) is more favorable for adsorption with the presence of water than the linear structure of G1.0-DETA.

Tab 4. Comparison of CO_2 adsorption capacity of amine functionalized fibrous sorbents.

Substrate	Grafted monomer	Amine	Temperature (°C)	p_{CO2} (atm)	Adsorption capacity (mmol/g)	Ref.
PP	GMA	Branched	30	0.10	5.53	This work
PP	GMA	PEI	25	0.10	2.51	14
PP	Am	PEI	25	0.10	5.91	14
PP	GMA	TETA	30	0.15	4.72	16
PAN	——[a]	Allylamine	22	0.15	6.22	15
Glass fiber	——[b]	PEI	30	0.24	4.12	13

[a] Allylamine was directly grafted onto the polyacrylonitrile fiber (PAN). [b] PEI was coated onto glass fiber by using epichlorohydrin as cross-linking agent.

Compared with other fibrous adsorbents reported (Tab 4), G3.0 showed relatively high adsorption efficiency, performing its possibility for practical application. More interestingly, Wu[14] has prepared a fibrous adsorbent (PP-GMA-PEI) through grafting GMA onto PP fiber, followed by reacting with PEI. Though PP-GMA-PEI has similar amine content to G3.0, its adsorption capacity was far below than G3.0's, further confirming the superiority of our route.

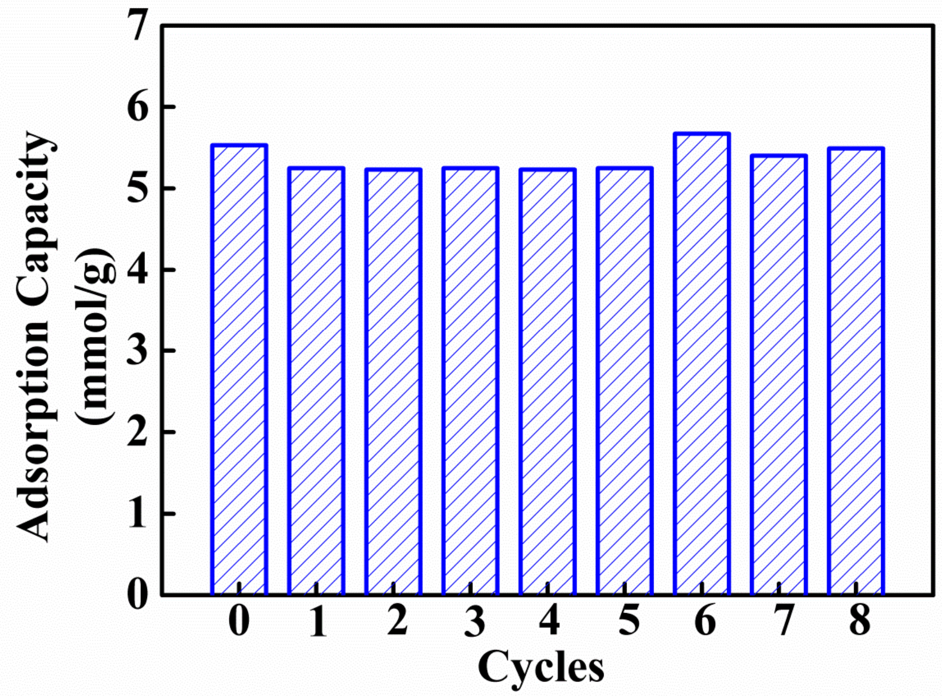


Fig 7. The regeneration performance of G3.0 fiber

In order to evaluate the regeneration performance of G3.0 fibers, 8 cycles of adsorption-desorption were carried out, and the result was shown in Figure 7. After 8 cycles, no significant decrease in CO_2 adsorption capacity was observed: the adsorption capacity of adsorbent could maintain above 99%. Furthermore, FT-IR spectra of the fresh and the regenerated G3.0 fiber were also presented in Figure 8. It was obvious that the regenerated fibers exhibited nearly the same spectra as the fresh. All these results confirmed that G3.0 fibers have great regeneration performance that is of great significance for practical application.

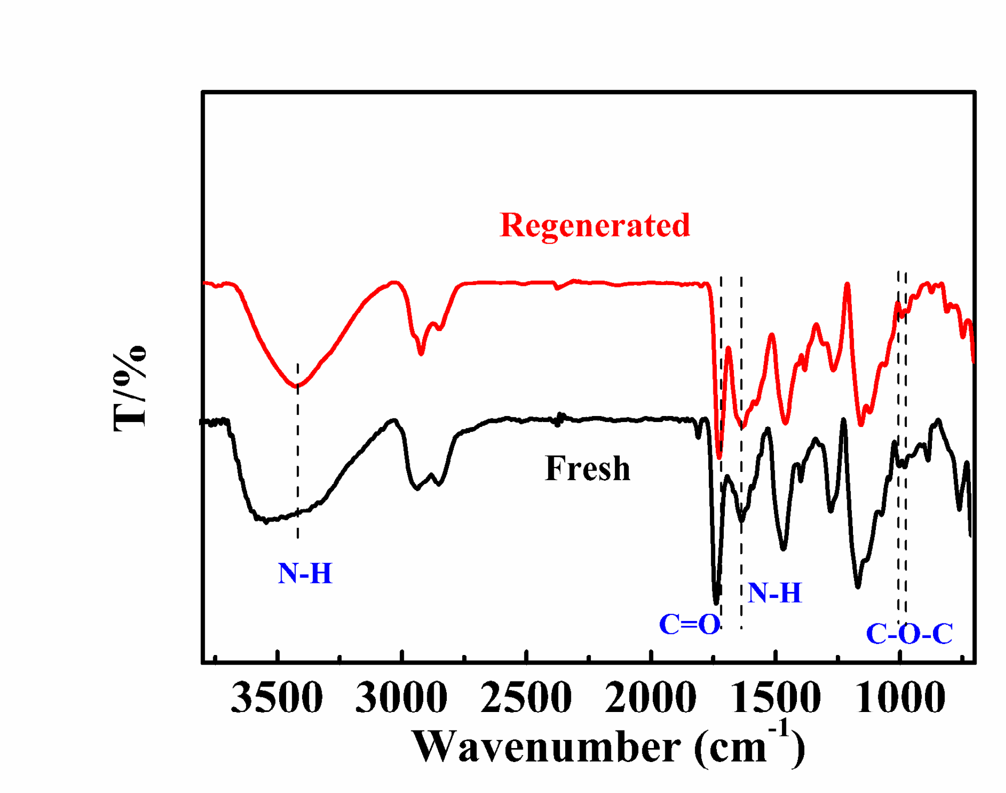


Fig 8. FT-IR spectra of the fresh and the regenerated G3.0 fibers

4. Conclusion

A polypropylene based hyperbranched absorbent fibers for CO_2 capture was prepared by co-irradiation grafting copolymerization of GMA onto PP fiber, followed by amination, hoffman alkylation and hydrolysis. The present work has shown that the adsorption performance of G2.0 and G3.0 has greatly been improved compared with G1.0, and the adsorption capacity of G2.0 and G3.0 were 5.35 mmol/g and 5.53 mmol/g at 30 ^{o}C, respectively. Particularly, the branched structure could promote the adsorption capacity and efficiency greatly due to its low mass transfer resistance of CO_2, more favorable than linear amination reagent. Furthermore, hyperbranched absorbent fibers could be easily and completely regenerated under mild conditions and are stable in the cyclic operations for 8 cycles.

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References

1. D. Aaron and C. Tsouris, *Sep. Sci. Technol.*, 2005, **40**, 321-348.

2. L. Espinal, D. L. Poster, W. Wong-Ng, A. J. Allen and M. L. Green, *Environ. Sci. Technol.*, 2013, **47**, 11960-11975.

3. L. Dumée, C. Scholes, G. Stevens and S. Kentish, *Int. J. Greenh. Gas. Con.*, 2012, **10**, 443-455.

4. U. Patil, A. Fihri, A. H. Emwas and V. Polshettiwar, *Chem. Sci.*, 2012, **3**, 2224-2229.

5. Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, *Ind. Eng. Chem. Res.,* 2010, **49**, 359-365.

6. A. Zhao, A. Samanta, P. Sarkar and R. Gupta, *Ind. Eng. Chem. Res.*, 2013, **52**, 6480-6491.

7. S. Hao, H. Chang, Q. Xiao, Y. Zhong and W. Zhu, *J. Phys. Chem. C*, 2011, **115**, 12873-12882.

8. F. Su, C. Lu, S. C. Kuo and W. Zeng, *Energ. Fuel.*, 2010, **24**, 1441-1448.

9. D. P. Bezerra, R. S. Oliveira, R. S. Vieira, C. L. Cavalcante Jr and D. C. S. Azevedo, *Adsorption*, 2011, **17**, 235-246.

10. M. Keramati and A. A. Ghoreyshi, *Physica E: Low-dimensional Systems and Nanostructures*, 2014, **57**, 161-168.

11. C. Zhang, W. Song, G. Sun, L. Xie, J. Wang, K. Li, C. Sun, H. Liu, C. E. Snape, T. Drage, *Energ. Fuel.*, 2013, **27**, 4818-4823.

12. W. J. Son, J. S. Choi, W. S. Ahn, *Micropor. Mesopor. Mat.*, 2008, **113**, 31-40.

13. P. Li, B. Ge, S. Zhang, S. Chen, Q. Zhang and Y. Zhao, *Langmuir*, 2008, **24**, 6567-6574.

14. Q. Wu, S. Chen, H. Liu, *RSC Adv.*, 2014, **4**, 27176-27183.

15. Y. Yang, H. Li, S. Chen, Y. Zhao and Q. Li, *Langmuir*, 2010, **26**, 13897-13902.

16. L. Zhuang, S. Chen, R. Lin and X. Xu, *J. Mater. Res.*, 2013, **28**, 2881-2889.

17. Y. H. Kim, *J. Polym. Sci. Pol. Chem.*, 1998, **36**, 1685-1698.

18. A. Sunder, M. Krämer, R. Hanselmann, R. Mülhaupt and H. Frey, *Angew. Chem. Int. Ed.*, 1999, **38**, 3552-3555.

19. J. Wang, C. Q. Li, J. Li and J. Z. Yang, *Sep. Sci. Technol.*, 2007, **42**, 2111-2120.

20. M. Badaničová, V. Zeleňák, *Monatshefte Fur Chemie*, 2010, **141**, 677-684.

21. H. Kassab, M. Maksoud, S. Aguado, M. Pera-Titus, B. Albela and L. Bonneviot, *RSC Adv.,* 2012, **2**, 2508-2516.

22. P. Lopez-Aranguren, L. F. Vega, C. Domingo, *Chem. Commun (Camb).*, 2013, **49**, 11776-11778.

23. J. H. Drese, S. Choi, R. P. Lively, W. J. Koros, D. J. Fauth, M. L. Gray and C. W. Jones, *Adv. Funct. Mater.*, 2009,**19**, 3821-3832.

24. K. Li, J. Jiang, F. Yan, S. Tian, and, X. Chen, *Appl. Energ.,* 2014, **136**, 750-755.

25. Z. Yao, H. Zhang, T. Dong and D. Yan, *Journal of Fudan University*, 1989, **28**, 34-38.

26. W. Zhang, S. Wang, J. Ji, Y. Li, G. Zhang, F. Zhang and X. Fan, *Nanoscale*, 2013, **5**, 6030-6033.

27. Y. Le, D. Guo, B. Cheng and J. Yu, *Appl. Surf. Sci.*, 2013, **274**, 110-116.

28. D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Edit.*, 2010, **49**, 6058-6082

29. S. Choi, J. H. Drese, C. W. Jones, *ChemSusChem*, 2009, **2**, 796-854