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OPEN Preparation and Properties of A **Hyperbranch-Structured Polyamine** adsorbent for Carbon Dioxide **Capture**

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A fibrous adsorbent with amino-terminated hyperbranch structure (PP-AM-HBP-NH2) was prepared by grafting hyperbranched polyamine (HBP-NH₂) onto the acrylamide-modified polypropylene (PP) fibers. The grafting of AM on PP fibers provided the active sites for introducing HBP-NH2 onto the PP fibers. This kind of "grafting to" procedure to synthesize hyperbranch-structured fiber could overcome the disadvantages of stepwise growth procedure, avoiding the complicated synthesis process and the requirement of strict experimental conditions. The grafted HBP-NH2 was three-dimensional dentritic architecture and had a large number of pores existing within the grafted polymers, which is favorable for CO₂ molecules to diffuse into the HBP-NH₂. Therefore, the as-prepared PP-AM-HBP-NH₂ fibers showed a high adsorption capacity (5.64 mmol/g) for CO₂ in the presence of water at 25 °C, and the utilization efficiency of alkyl amino groups could reach 88.2%, demonstrating that the hyperbranched structure of adsorbents can greatly promote adsorption capacity and efficiency. This could be attributed to better swelling properties and lower mass transfer resistance to CO₂ of the hyperbranched adsorbent. PP-AM-HBP-NH₂ also showed excellent regeneration performance, and it could maintain the same adsorption capacity for CO₂ after 15 recycle numbers as the fresh adsorbent.

Great energy demand intensifies the combustion of fossil fuels (coal, petroleum and natural gas), resulting in escalated global CO₂ emission, which is one of the major causes of global warming. One efficient way to control atmospheric CO₂ concentration is to reduce CO₂ emission from flue gas which takes up 86% of anthropogenic greenhouse gas¹. The two main methods to capture CO₂ from the flue gas are physical or chemical absorption and adsorption. Though absorption, using aqueous solvents, has many advantages, such as higher selectivity and absorption capacity for CO2 removal from flue gas, it has drawbacks like high volatility leading to absorbent consumption, high alkalinity causing equipment erosion and high energy consumption for regeneration². In contrast, solid adsorbents overcome these disadvantages and exhibit promising application in carbon capture.

Among solid adsorbents, solid amine adsorbents such as amino-functionalized MCM-41³, SBA-15^{4,5}, Zeolite 13X^{6,7} and activated carbon^{8,9} have been used, having attracted much attention due to their physical and chemical adsorption of CO₂. Solid amine adsorbents have advantages such as lower energy consumption for regeneration, higher adsorption capacity and efficiency, higher stability and less erosion for equipments. However, large amount of amine loading on these porous supports, particularly microporous and mesoporous silica supports may cause serious pore blockage and CO₂ diffusion resistance, leading to the reduction of adsorption capacity for CO₂¹⁰. Thus, it is necessary to choose another support instead of porous supports to retain the adsorption capacity while increasing the loads of amino.

Nowadays, Fibrous adsorbents have gained much attention due to their light weight, great mechanical property, large external surface area, short transit distance, low pressure drops, and flexibility. Lots of works about fibrous adsorbents have done in our group 10-14. Li11 chose epichlorohydrin as cross-linking reagent to graft PEI onto glass fiber (GF) and prepared GF-PEI adsorption fiber with an adsorption amount of 4.12 mmol/g. Yang¹² adopted (NH₄)₂S₂O₈/NaHSO₃ redox as initiator reagent to graft allylamine onto polyacrylonitrile (PAN) and

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(a)
$$H_{3}CO O H_{2}NH_{2}NH_{2}NH_{2}$$

$$H_{2}N NH_{2} H_{3}NH_{2}$$

$$H_{3}CO O H_{3}NH_{2} H_{3}NH_{2}$$

$$H_{3}CO O H_{3}NH_{2} H_{3}NH_{2}$$

$$H_{3}CO O H_{3}NH_{2} H_{3}NH_{2}$$

$$H_{3}CO O H_{3}NH_{3}NH_{2}$$

$$H_{3}CO O H_{3}NH_{3}NH_{4}NH_{5}NH_{2}$$

$$H_{3}CO O H_{3}NH_{5$$

Figure 1. Reaction scheme of HBP-NH₂ preparation (a) and PP-AM-HBP-NH₂ preparation (b).

gained PAN-AF fiber with an adsorption amount of 6.22 mmol/g when the grafting degree was 60.0 wt%. These fibers all have great regeneration abilities. Besides the substrate, the amino content and the structure of amino of the adsorbents are the important factors that affect the $\rm CO_2$ adsorption performance of the adsorbents. $\rm Xu^{15}$ has developed a new procedure that is effective and safe to synthesize hyperbranch-structured fiber by stepwise growth using N-(2-chloroethyl)-benzaldimine as monomer. The maximum adsorption capacity of hyperbranched solid amine fiber reaches 5.53 mmol/g at 30 °C. These results demonstrate that hyperbranched structure can significantly increase the adsorption capacity and efficiency. However, this kind of stepwise growth procedure is complicated and requires strict experimental conditions because of its multiple steps.

Amino-terminated hyperbranched polyamine is easier to prepare compared with dendritic molecules, because it doesn't require uniform structure and high symmetry^{16–23}. Moreover, there are abundant amino groups which can be the adsorption sites of CO₂ in the hyperbranched polyamine. Using hyperbranched polyamine as animation reagent is a promising way to prepare hyperbranch-structured adsorbents with high CO₂ adsorption capacity.

In this study, a simple procedure has been developed for the synthesis of hyperbranch-structured fibers, in which the amino-terminated hyperbranched polyamine (HBP-NH $_2$) was first prepared through Michael addition reaction of pentaethylenehexamine (PEHA) and methyl acrylate (MA), and then grafted onto acrylamide (AM)-modified polypropylene (PP) fibers (Figs 1 and 2). The chemical structure, adsorption property and regeneration ability of the PP based amino-terminated hyperbranch-structured fiber (PP-AM-HBP-NH $_2$) were evaluated in detail.

Results and Discussion

Control of amino density of PP-AM-HBP-NH₂ adsorbent. The HBP-NH₂ with high amino density was prepared through Michael addition reaction of PEHA and MA. The molecular weight and amino content of the HBP-NH₂ were listed in Table 1.

As shown in Table 1, molecular weight and nitrogen content of HBP-NH $_2$ were 10820 g/mol and 30.29 wt%, respectively, and the alkyl amino content could reach 18.01 mmol/g.

HBP-NH₂ was combined onto AM-grafted PP fiber (PP-AM) through the reaction of amide on PP-AM and amino groups on HBP-NH₂. As shown in Fig. 3, with the increase of HBP-NH₂ concentration in the synthesis system, more and more HBP-NH₂ was combined onto PP fiber, thus, the nitrogen content and alkyl amino content of the prepared PP-AM-HBP-NH₂ increased. When the concentration of HBP-NH₂ was 80%, the nitrogen content could reach to 18.45 wt%. Whereafter, the nitrogen content and alkyl amino content didn't increase with the further increase of the HBP-NH₂ concentration. Increasing HBP-NH₂ concentration would provide more amino groups that could be grafted onto PP-AM fibers, however, when HBP-NH₂ concentration exceed a certain

preparation (b)

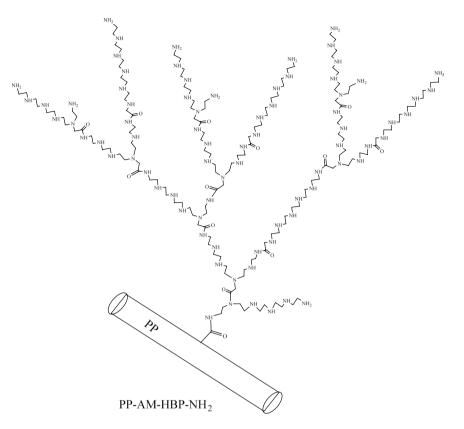


Figure 2. A possible structure of PP-AM-HBP-NH₂.

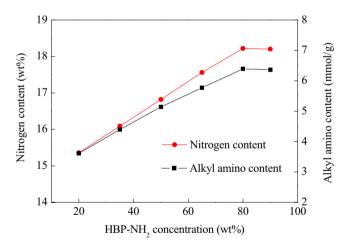


Figure 3. Nitrogen content and alkyl amino content of PP-AM-HBP-NH $_2$ prepared in various concentration of HBP-NH $_2$.

Mw (g/ mol)	C (wt%)	N (wt%)	H (wt%)	O (wt%)	Amino amount (mmol/g)	Amide content (mmol/g)	Alkyl amino content (mmol/g)
10820	50.98	30.29	12.93	5.80	21.64	3.63	18.01

Table 1. Molecular weight and amino content of HBP-NH $_2$ where the amide content (mmol/g) of HBP-NH $_2$ was calculated from the oxygen mole content, alkyl amino content of HBP-NH $_2$ was calculated by subtracting the amide content from total amino amount.

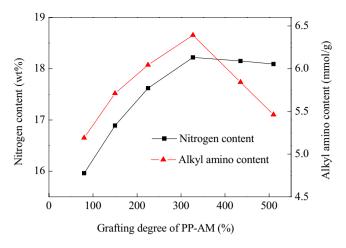


Figure 4. Nitrogen content and alkyl amino content of PP-AM-HBP-NH₂ prepared by using PP-AM with various grafting degree.

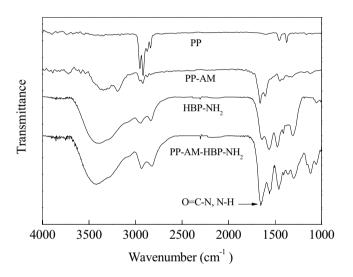


Figure 5. FT-IR spectra of PP, PP-AM, HBP-NH₂ and PP-AM-HBP-NH₂.

value (80 wt% in this case), viscosity of the reaction system increased and the mobility decreased, which would reduce diffusion and mass transfer of the HBP-NH₂ molecules, thus decrease the amount of grafted HBP-NH₂.

In order to provide reactive sites to combine HBP-NH₂, AM was firstly grafted onto PP fiber by simultaneous grafting copolymerization. The effect of the grafting degree of AM on the amino density of the prepared PP-AM-HBP-NH₂ was examined. As shown in Fig. 4, the nitrogen content of PP-AM-HBP-NH₂ increased with the grafting degree of PP-AM till the grafting degree was 320%. Accordingly, the alkyl amino content of PP-AM-HBP-NH₂ also increase with grafting degree of PP-AM, however, it decreased after the grafting degree of PP-AM was 320%. The nitrogen content and alkyl amino content reached their maximum values (18.22 wt%, 6.39 mmol/g, respectively.) when the grafting degree of PP-AM was 320%. As we know, amount of amide groups on PP-AM increased in proportion to its grafting degree, amide groups could react with HBP-NH₂ by amide substitution reaction, thus the more the amide groups, the higher the nitrogen content and alkyl amino content. However, with the increase of grafting degree of PP-AM, the grafting layer on the surface of PP fibers became thicker, which was not beneficial for HBP-NH₂ molecules to diffuse into the internal layer and react with the amide groups inside. Therefore, nitrogen content didn't further increase with the grafting degree, and the proportion of alkyl amino content would decrease due to the unreacted amide.

Morphology and Chemical characterization. Figure 5 showed FT-IR spectra of PP, PP-AM, and PP-AM-HBP-NH₂, respectively. Compared with the spectra of PP fibers, the PP-AM fibers were characterized by the peaks at 1653 cm⁻¹ and 1606 cm⁻¹ corresponding to the stretching vibrations of C=O and -NH, which proved the existence of amide bond. Two broad adsorption peaks at 3000–3500 cm⁻¹, which are attributed to primary amino, were observed. The existence of amide bonds and primary amino confirmed that AM had successfully grafted on PP fibers. The absorption peaks at 1573 cm⁻¹, 1460 cm⁻¹, and 1116 cm⁻¹ in the spectrum of HBP-NH₂ are corresponding to the bending of amino groups (N-H) in HBP-NH₂. The wide absorption peak at 3000–3500 cm⁻¹ in the spectrum of PP-AM-HBP-NH₂ is corresponding to the N-H bond of primary amino; the

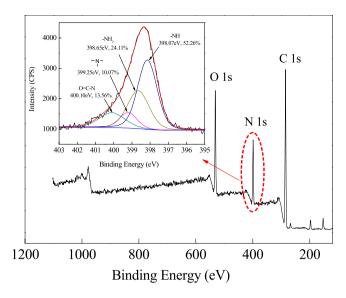


Figure 6. N1s peak processing of XPS of PP-AM-HBP-NH₂.

absorption peaks at $2820\,\mathrm{cm^{-1}}$ and $2928\,\mathrm{cm^{-1}}$ are corresponding to symmetric and asymmetric stretching vibrations of $-\mathrm{CH_2-}$, respectively. The peaks at $1653\,\mathrm{cm^{-1}}$ and $1573\,\mathrm{cm^{-1}}$ are assigned to the stretching vibrations of C=O and N-H, respectively, which represented the existence of amide bond. The absorption peaks at $1573\,\mathrm{cm^{-1}}$, $1460\,\mathrm{cm^{-1}}$, and $1116\,\mathrm{cm^{-1}}$ are corresponding to the bending of amino groups (N-H) in PP-AM-HBP-NH₂. These results testified the substituting of HBP-NH₂ for amino groups in amide.

The nitrogen-containing groups were further resolved into amide and alkyl amino (including 1, 2, 3° amino) by N1s peak processing of XPS spectrum, which were showed in Fig. 6. It could be resolved into four peaks at $400.10\,\mathrm{eV}$ (13.56%), 399.25 eV (10.07%), 398.65 eV (24.11%), and 398.07 eV (52.26%), these peaks were the characteristics of amide, tertiary amino, primary amino, and secondary amino, respectively. The presence of tertiary amino indicated that the HBP-NH₂ was grafted onto the PP-AM, and the target hyperbranch-structured fibers were successfully prepared.

During the grafting of AM onto PP fibers, AM copolymerized with PP to form PP-AM copolymers with polyamide oligomer as side chains 24 , the diameter of the PP-AM thus was increased to 95.52 μ m from 54.11 μ m (PP). And then its diameter further increased to 116.23 μ m after grafting HBP-NH $_2$ onto PP-AM (Figure S1 of the supporting information). As shown in Fig. 7, no significant changes in diameter of PP fiber were observed after swelling in water at 25 °C, the swelling degree was only 0.8% due to the hydrophobicity of PP fiber. However, under moisture condition, PP-AM-HBP-NH $_2$ could present good swelling property, its diameter increased from 116.23 μ m under dry condition to 211.18 μ m in the presence of water, the swelling degree was 81.69% in the presence of water at 25 °C, which would be beneficial to the diffusion of CO $_2$ into the internal layer.

Adsorption property of PP-AM-HBP-NH₂. Effect of alkyl amino content. As shown in Fig. 8, The $\rm CO_2$ adsorption capacities and alkyl amino utilization efficiencies almost linearly increased with alkyl amino content. However, when HBP-NH₂ grafting layer became thicker and thicker film-diffusion resistance became the key factor affecting the adsorption kinetics of $\rm CO_2$. Moreover, the number of the accessible adsorption groups would be reduced when the grafting layer of HBP-NH₂ was too thicker. It was further verified by swelling property analysis (Fig. 9), the diameters of PP-AM-HBP-NH₂ in both dry and moisture conditions increased with its alkyl amino content, but the swelling degree showed a decrease tendency. When alkyl amino content exceed 6.39 mmol/g, the swelling degree decreased sharply, which would greatly limit diffusion of $\rm CO_2$ into the internal layer, thus lead to the decrease of the adsorption capacity and alkyl amino utilization efficiency.

Effect of adsorption temperature. The results in Fig. 10 indicated that CO_2 could be completely adsorbed by PP-AM-HBP-NH₂ adsorbent at the early stage. It lasted for longer time for the complete adsorption of CO_2 under low temperature. Increasing adsorption temperature would accelerate the breakthrough of CO_2 from the adsorption bed. Table 2 showed that the adsorption capacity was higher at lower adsorption temperature. The CO_2 adsorption capacity of PP-AM-HBP-NH₂ at 10 °C could reach 5.90 mmol/g, which was two times as much as that at 80 °C (2.82 mmol/g). Low temperature was beneficial to the adsorption of CO_2 on solid amine adsorbent because it was an exothermic process.

Unlike the linear amination reagents, HBP-NH $_2$ possess three-dimensional dentritic architecture and a large number of pores exist within the grafted oligomers 10 , 11 , 13 , the average diameter of pore is $0.5 \, \mathrm{nm}^{16}$ (greater than that of CO $_2$ molecular diameter (0.33 nm)). This kind of pores is favorable for CO $_2$ molecules to diffuse into the internal layer and react with the amino groups inside, and therefore greatly promote the adsorption capacity and amino utilization efficiency (Table 2). Moreover, the single branched molecule chain of HBP-NH $_2$ would provide various amino adsorption sites for CO $_2$ capture, and the amino groups can fully contact with CO $_2$ molecules. Thus alkyl amino utilization efficiency of PP-AM-HBP-NH $_2$ could reach 88.2% at 25 °C, which was much higher than that of the other linear amine reagents (Table 3).

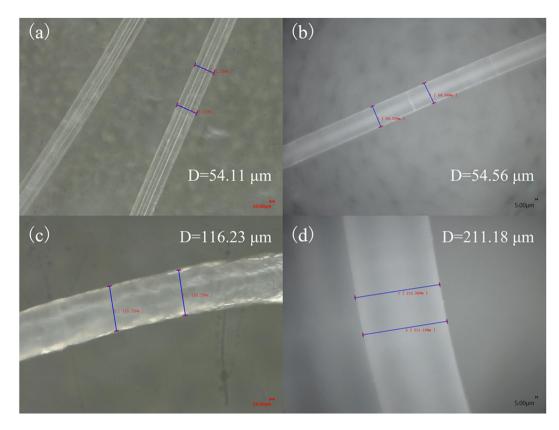


Figure 7. Ultra-depth three-dimensional microscope images of PP (a,b) and PP-AM-HBP-NH₂ (c,d) under dry (left) and moisture (right) conditions.

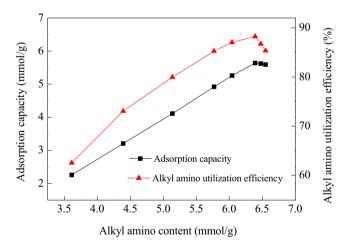


Figure 8. Effects of alkyl amino content on adsorption capacity of PP-AM-HBP-NH₂.

Compared with other fibrous adsorbents reported (Table 3), PP-AM-HBP-NH₂ adsorption fibers showed relatively high adsorption efficiency. More interestingly, Wu¹⁰ has prepared a fibrous adsorbent (PP-AM-PEI) through grafting AM onto PP fibers, followed by reaction with PEI. Though PP-AM-PEI had a similar adsorption capacity with PP-AM-HBP-NH₂ adsorption fibers, its amino utilization efficiency (56.0%) was much lower than that of PP-AM-HBP-NH₂, further highlighting the superiority of PP-AM-HBP-NH₂ adsorbent.

Regeneration performance of PP-AM-HBP-NH₂. The PP-AM-HBP-NH₂ adsorbent was processed for 15 cycles of adsorption (at 25 °C) -desorption (at 90 °C), and the results were shown in Fig. 11. After 15 cycles, no significant changes in CO_2 adsorption capacities were observed, and the adsorption capacity of regenerated PP-AM-HBP-NH₂ remained at 5.60 ± 0.1 mmol/g (Fig. 11 inset). It was evident that the hyperbranch-structured adsorbent could remain stability after multiple regeneration cycles and maintain its adsorption capacity for CO_2 .

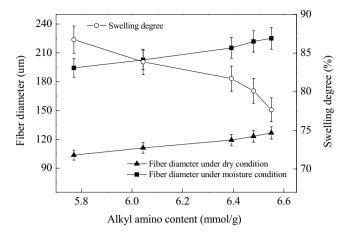


Figure 9. Diameter and swelling degree of PP-AM-HBP-NH₂.

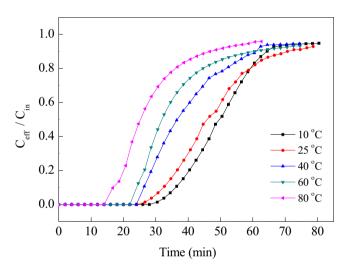


Figure 10. Breakthrough curves of CO₂ adsorption on PP-AM-HBP-NH₂ at different adsorption temperatures (alkyl amino content of PP-AM-HBP-NH₂ was 6.39 mmol/g).

Temperature (°C)	Adsorption capacity (mmol/g)	Alkyl amino utilization efficiency (%)
10	5.90	92.3
25	5.64	88.2
40	4.80	75.1
60	3.81	59.6
80	2.82	44.1

Table 2. Adsorption capacities and alkyl amino utilization efficiency of PP-AM-HBP-NH₂ fibers (alkyl amino content was 6.39 mmol/g) at different adsorption temperatures.

Conclusions

A fibrous adsorbent with amino-terminated hyperbranch structure (PP-AM-HBP-NH₂) could be conveniently prepared by grafting hyperbranch oligomers HBP-NH₂ onto acrylamide modified polypropylene fibers. This study showed that the PP-AM-HBP-NH₂ fibers could effectively adsorb $\rm CO_2$ due to its high amino density and hyperbranch structure, the maximum $\rm CO_2$ adsorption capacity and amino utilization efficiency of PP-AM-HBP-NH₂ could reach 5.64 mmol/g and 88.2%, respectively. The hyperbranched structure as well as the good swelling properties of the grafted HBP-NH₂ could provide more active sites for $\rm CO_2$ adsorption and reduced the mass transfer resistance to $\rm CO_2$, thus remarkably enhance the adsorption ability and amino utilization efficiency of the adsorbent. The prepared PP-AM-HBP-NH₂ adsorbent also showed excellent regeneration stability, it could maintaine almost the same $\rm CO_2$ adsorption capacity after 15 cycles of adsorption-desorption.

Substrate*	Grafted monomer**	Amine	Adsorption capacity (mmol/g)	Amino utilization efficiency (%)	Ref.
PP	AM	HBP-NH ₂	5.64	88.2	This work
PP	AM	PEI	5.91	56.0	10
GF	ECH	PEI	4.12	57.0	11
PP	GMA	TETA	4.72	46.1	13
VF	AM	TEPA	1.92	40.4	14
VF	AM	EDA	2.82	60.1	14

Table 3. Comparison of CO₂ adsorption capacity of amine functionalized fibrous sorbents (adsorption temperature: 25 °C, CO₂ concentration: 10%). *GF: glass fibers, VF: viscose fibers, ** ECH: epichlorohydrin, GMA: glycidyl methacrylate.

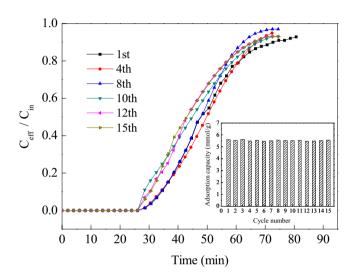


Figure 11. Breakthrough curves of CO_2 adsorption on fresh and regenerated adsorbents (alkyl amino content was 6.39 mmol/g) and the CO_2 adsorption capacities (inset).

Experimental Section

Materials and reagents. All reagents were purchased as analytical grade (AR) and used without further purification. Polypropylene (PP) fibers were provided by Xinshun Special Fiber Company (Zhongshan, China). Pentaethylenehexamine (PEHA) was purchased from Guangzhou Reagent Company. Acrylamide (AM), ethanol and ammonium ferrous sulfate [(NH₄)₂SO₄·FeSO₄·6H₂O)] were purchased from Tianjin Fuchen Chemical Reagents Factory.

Preparation of hyperbranch-structured fibers. Synthesis of HBP-NH₂. The preparation process of HBP-NH₂ was illustrated in Fig. 1(a). In a typical process, 0.5 mol PEHA was dissolved in 50 mL anhydrous methanol at 0 °C under N₂ atmosphere. 0.5 mol MA dissolved in 50 mL anhydrous methanol was added dropwise to the above PEHA solution. PEHA reacted with MA through Michael addition reaction to produce a light yellow liquid intermediate (addition product). The intermediate was transferred to a round bottom flask in a rotary evaporation apparatus, and heated at 60 °C for 1 h to remove methanol solvent; then it was kept at 100 °C for 2 h for condensation reaction. After that, the reaction temperature was elevated to 140 °C and kept for 2 h for the completion of the self-condensation. The generated methanol in the reaction was removed by rotary evaporation in vacuum. The obtained amino-terminated hyperbranched polyamine was denominated as HBP-NH₂.

Synthesis of PP-AM-HBP-NH₂. The preparation process of PP-AM-HBP-NH₂ was illustrated in Fig. 1(b). In a typical synthesis procedure: firstly, PP was subjected to γ -ray irradiation at a dosage rate of 0.837 kGy/h to obtain preirradiated PP fibers. Then AM was grafted onto PP fibers by the following procedure¹⁰: 85 g H₂O and 0.08 g (NH₄)₂SO₄·FeSO₄·6H₂O were put in a 100 mL three-necked flask, and oxygen in the solution was removed by purging nitrogen for 30 min, then 1.00 g of PP fibers and 15.00 g of AM were put into the flask and the grafting reaction lasted for 2 h at 70 °C. After the grafting step, the fibers were washed with boiling deionized water for several times to completely remove residual monomers and homopolymers, and the AM-grafted fibers PP-AM was dried in vacuum at 60 °C for 24 h²⁴⁻²⁶. Afterwards, HBP-NH₂ was introduced onto PP-AM fibers by reacting with HBP-NH₂ (20–90 wt% aqueous solution) for 6 h. The obtained fibers PP-AM-HBP-NH₂ was rinsed with deionized water and ethanol, and dried at 60 °C for 24 h. The grafting degree of PP-AM (G_{AM} , %) was calculated by the following Eq. (1):

$$G_{AM} = \frac{W_2 - W_1}{W_1} \times 100\% \tag{1}$$

where W_1 and W_2 are the weights (g) of PP and PP-AM, respectively.

Alkyl amino content (n, mmol/g) of PP-AM-HBP-NH2 (amide excluded) was calculated by Eq. (2):

$$n = \frac{n_2 W_3 - n_1 W_2 n_0 (W_3 - W_2)}{W_3} \tag{2}$$

where n_0 and n_1 are the amide content (mmol/g) of HBP-NH₂ and PP-AM, respectively, n_2 is the amino content (mmol/g) of PP-AM-HBP-NH₂, W_3 is the weight (g) of PP-AM-HBP-NH₂.

Since the preparation of HBP-NH₂ is multi-step and the reaction sites are non-unique, structures of products could be various. Based on the preparation principle of PP-AM-HBP-NH₂, a possible structure of PP-AM-HBP-NH₃ is illustrated in Fig. 2.

Physical and chemical characterization. Elemental analysis (Elementar, Vario EL), Infrared (IR) spectra (Tensor-27 spectrometer) and X-ray photoelectron spectroscopy (ESCALAB 250, Thermo-VG Scientific) were employed to determine the composition and chemical structures of different samples, which were extracted by using ethanol^{24,27}. High performance liquid chromatograph (Waters 600), and gel column (TSK-GEL G2000 SW XL, 7.8 mm \times 300 mm) were employed to determine the molecular weight of HBP-NH₂NH₂. Test conditions: mobile phase was phosphate buffer (pH = 7.0); detection wavelength was set at 222 nm; flow rate was 0.5 mL/min; column temperature was 300 °C; injection volume was 10 uL.

Ultra-depth three-dimensional microscope (VHX-1000C) was employed to observe the morphology and measure the diameter of fibers. The swelling degree (Sd, %) was calculated as follows:

$$Sd = \frac{D_2 - D_1}{D_1} \times 100\% \tag{3}$$

where D_1 and D_2 are the diameter of fibers in dry conditions and after swelling in water at 25 °C, (μ m), respectively.

 CO_2 adsorption experiment. Breakthrough curves were used to characterize the CO_2 adsorption performances of all samples in the presence of water. 1.00 g adsorbent sample was tightly packed in an glass column ($\Phi=1.3$ cm), into which a dry nitrogen flow was introduced at a flow rate of 30 mL min $^{-1}$ for 0.5 h to remove the air and excess water in the column. Then, the dry CO_2/N_2 mixed gas (CO_2 : $N_2=1:9$ (volume ratio)) was introduced through the column at a flow rate of 30 mL/min. The inlet/outlet concentrations of CO_2 were analyzed every two minutes, using a Techcomp 7900 gas chromatograph equipped with a thermal-conductivity detector (TCD). The effect of adsorption temperature on the adsorption was investigated in the range of 10 to 80 °C. After adsorption, pure nitrogen gas at a flow rate of 30 mL/min was introduced through the tube at 90 °C to regenerate the spent adsorbent sample.

The adsorption capacity was calculated as follows:

$$Q = \int_0^t (C_{\rm in} - C_{\rm eff}) V dt / 22.4W$$
(4)

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

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Author Contributions

Shuixia Chen and Hui He designed the structure of the adsorbent, proposed the synthesis strategy, and wrote the manuscript. Hui He, Yajie Hu, Qinghua Wu have prepared the hyperbranch-structured polyamine adsorbent and evaluated the properties and adsorption performance. Linzhou Zhuang and Beibei Ma help to revise the manuscript.

Additional Information

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