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Introduction

Carbon black is a particulate form of elemental carbon produced by thermal decomposition or incomplete combustion of gaseous or liquid hydrocarbons under controlled conditions.¹ Carbon black consists of structurally complex particles with predominantly spherical or ellipsoidal shapes formed by aggregation of graphitic layer planes with both amorphous and crystalline substructures.² The structure of carbon black differs from other forms of bulk carbon such as graphite, charcoal, cokes, and diamond in that carbon blacks are particulates made of aggregates with complex compositions.³ Carbon black has

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Carbon black functionalized with hyperbranched polymers: synthesis, characterization, and application in reversible CO₂ capture[†]

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The functionalization of carbon black by grafting of hyperbranched polymers from the surface via selfcondensing atom transfer radical polymerization (SC-ATRP) is reported. The surfaces of the pristine carbon black were modified with ATRP initiators using two different methods. The first method uses acid oxidation to place COOH groups on the carbon black surface, followed by the esterification to give ATRP initiators bound to the carbon black surface. Alternatively, ATRP initiators bearing both azido and bromine groups were placed directly on the carbon black surface by nitrene chemistry. The hyperbranched poly(pchloromethylstyrene) (PCMS) was grafted from the ATRP initiator modified carbon black surfaces using the inimer of p-chloromethylstyrene, and CuCl/CuCl₂/N,N,N',N'',Pentamethyldiethylenetriamine (PMDETA) as the catalytic system in N,N-dimethylformamide (DMF). In addition, a one-pot two-step method was developed to graft crosslinked polymers from the carbon black surfaces. The polymerization process was well controlled and the fraction of the grafted polymers on carbon black could be adjusted by changing the polymerization time. The resulting samples were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The hyperbranched polymers on the carbon black surfaces were quaternized to give an ammonium group on the polymer, and a chloride counterion was subsequently exchanged to give a hydroxide counterion. Under these basic conditions, the ATRP initiators should be attached to the surface using nitrene chemistry rather than acid oxidation, to avoid the hydrolysis of the ester groups that link the grafted polymers to the carbon black surface. The ammonium hydroxide functionalized carbon black materials were utilized for the reversible absorption and desorption of CO₂ from ambient air, providing improved absorption/desorption kinetics compared with the commercially available Excellion membrane.

> many useful properties, such as high electrical conductivity, low thermal expansion, environmental stability, and low cost, generating many applications in a variety of fields, including reinforcing agents in rubber applications, pigments in plastics, inks, and coatings.⁴ Many of these applications involve dispersing carbon black into either polymeric systems or solvents, but since crude carbon black is difficult to disperse in solvents, the surface modification of carbon black is often used to improve the dispersibility. For instance, crude carbon black is difficult to disperse in water, whereas carbon black can be dispersed in aqueous phase via the adsorption of surfactants.⁵ Furthermore, attaching polymers to the surface of carbon black markedly improves the dispersibility in solvents and compatibility in polymer matrices. In addition, surface grafting can introduce various functional groups onto the surface, including photosensitive, bioactive, and amphiphilic groups.6

> There are two methods to covalently bond polymers to the surface of carbon black, the "grafting onto" and "grafting from". "Grafting onto" involves the synthesis of a polymer with a reactive end-group and then attaching the polymer to the

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surface of carbon black using the reactive end-group. One limitation of the grafting-onto approach is that the polymers already grafted onto the surface hinder the approach of the subsequent polymers, placing a limit on the attainable grafting density.⁷ "Grafting from" involves the modification the surface with initiators, followed by the growth of polymers from the surface. Since small molecules have much less steric hindrance than polymers, it is easier to create densely grafted surfaces by this approach.⁸

Both techniques have been used to functionalize carbon black surfaces. One interesting example used the "grafting onto" approach used the carbon black surface to trap polymeric radicals generated by the thermal dissociation of nitroxide-terminated polymers, obtained by nitroxide-mediated radical polymerization (NMP).9 This method was used to introduce various polymers onto the carbon black surfaces, including polystyrene, poly(4-acetoxystyrene), poly(4-hydroxystyrene), (4-acetoxystyrene)-block-polystyrene, poly(4-hydroxystyrene)-block-polystyrene, and polycaprolactone,^{2a,9,10} as well as poly(4-vinylpyridine), poly(styrene-co-maleic anhydride), and poly(styrene-co-(4-vinylpyridine)).11 In addition, carbon black has been functionalized by polymeric radicals formed by thermal decomposition of azo- and peroxy-functional molecules, as well as macroradicals derived from the redox reaction between polymers having hydroxyl groups and ceric ions.11

Similarly, polymers have been grafted from carbon black using anionic,¹² cationic,¹³ and radical polymerization.¹⁴ For example, hydroxymethyl groups were introduced onto pristine carbon black surfaces by reacting the unsaturated hydrogen atoms present in the polycondensed aromatic rings of carbon black with formaldehyde under alkaline conditions.^{13b} These hydroxymethyl groups were used as initiating sites in the grafting of multihydroxyl hyperbranched polyethers from the carbon black surface by cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)-oxetane.13b Unlike cationic or anionic reactions, radical polymerization is tolerant towards various functional groups and impurities. However, conventional radical polymerization offers minimal control over molecular weights and molecular weight distributions of the polymers. Therefore, reversible-deactivation radical polymerization (RDRP) can be used to graft polymers with controlled molecular weight and topology from the carbon black surface.15 Atom transfer radical polymerization (ATRP) is a versatile RDRP method, which has been used to prepare polymers with complex architectures as well as polymer brushes on organic/ inorganic substrates.16

Previously, poly(*n*-butyl acrylate) (poly(*n*-BA)) was grafted from carbon black surfaces bearing ATRP initiating sites, giving hybrid particles that showed excellent dispersibility and stability in good solvents for poly(*n*-BA).⁸ Subsequently, a block of *tert*-butyl acrylate (*t*-BA) was grown from poly(*n*-BA) functionalized carbon black, yielding a water-dispersible carbon black composite after cleavage of the *tert*-butyl groups to form poly(acrylic acid) grafted segments.¹⁷ ATRP has also been used to graft polystyrene (PS), poly(methyl methacrylate) (PMMA),¹⁸ and responsive polymers, such as pH-responsive 2-(dimethylamino)ethyl methacrylate (DMAEMA)¹⁹ and temperatureresponsive poly(*N*-isopropylacrylamide) (PNIPAAm),²⁰ from the surface of carbon black. A comb-structured polymer-grafted carbon black was synthesized by a combination of SI-ATRP of 2hydroxyethyl methacrylate and ring-opening polymerization of ε -caprolactone.²¹

The possibility of introducing various functional polymers onto the surface of carbon black makes the resulting hybrid materials useful for various applications. One of the most important potential applications is to mitigate the effects of climate change associated with rising carbon dioxide (CO_2) level in the atmosphere.22 Various strategies have been developed, including carbon capture and sequestration (CCS), which focuses on the capture of CO₂ emitted from burning fossil fuels.²³ Recently, "CO2 air capture" has emerged as a promising methodology that captures CO₂ directly from air.²⁴ One of the most environmentally promising methods for CO₂ air capture is the humidity swing proposed by Lackner et al.25 In the humidity swing, CO₂ is captured under dry conditions, and released under humid conditions by the interchange of carbonate and bicarbonate anions. Under dry conditions, the bicarbonate ion is favored, and one carbonate ion absorbs one CO₂ and one water molecule to give two bicarbonate ions, and the reverse reaction occurs under wet conditions. In addition, a hydroxide functionalized resin undergoes a onetime absorption of CO2 to generate the bicarbonate ion, which participates in the humidity swing. Resins bearing quaternary ammonium hydroxide groups have been used to reversibly capture CO2 from ambient air utilizing the humidity swing.^{25a,b} However, these resins generally have a relatively low surface area and dense structures, implying that higher capacities and faster kinetics could be achieved by increasing the surface area and gas diffusion rates. Recently, our group investigated porous polymers and high surface area supports, including carbon black, in the humidity swing.^{25c,d} These porous materials showed an order of magnitude improvement in the kinetics of CO₂ absorption and desorption, and a 2-4 fold improvement in the amount of CO2 absorbed per cycle.25c,d

Carbon black is a promising candidate as the support material for CO₂ capture, since there are several potential advantages for polymer-grafted carbon black: (1) carbon black has a large specific surface area in the range of 50 $m^2 g^{-1}$ to 1000 m² g⁻¹;²⁶ (2) carbon black is inexpensive and available in large quantities, which facilitates industrial applications;²⁷ (3) carbon black has high chemical and thermal stability, since it contains 97-99% of elemental carbon;²⁸ and (4) well-defined polymers can be grafted from carbon black and a desired percentage of polymer grafting can be achieved by controlled surface-initiated polymerization. This paper gives various procedures for the self-condensing atom transfer radical polymerization (SC-ATRP) of p-chloromethylstyrene (CMS), giving hyperbranched polymers grafted from the carbon black surface. This paper also outlines how the hyperbranched polymers can be functionalized to quaternary ammonium hydroxide groups, which can reversibly capture CO₂ through the humidity swing.

Results and discussion

1 Functionalization of carbon black with ATRP initiators

ATRP initiators have to be anchored onto the surface of carbon black to use the "grafting from" approach. There are three commonly used methods to covalently bind ATRP initiators onto carbon materials (including carbon black, carbon nanoonions, CNTs, and graphene): acid oxidation,²⁹ nitrene chemistry,³⁰ and Pschorr-type arylation.³¹

The acid oxidation method was initially used to modify the carbon black surface with an ATRP initiator. As shown in Scheme 1a, the carboxyl group modified carbon black (CB-COOH) was prepared by acid oxidation. Then, an acyl chloride group modified carbon black (CB-COCl) was prepared by reacting CB-COOH with SOCl₂. Finally, the CB-COCl was reacted with 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) to form carbon black modified with ATRP initiators (CB-Br). The Br content in CB-Br was 0.63 mmol g^{-1} , as determined by elemental analysis. TGA curves (Fig. 1) were obtained from 50 to 570 °C under a flow of nitrogen at a heating rate of 10 °C min⁻¹. The pristine carbon black (CB) remained stable to 570 °C, with only 1.7% weight loss. The CB-COOH sample had no distinguishable main weight loss region, and had 17.8% weight loss below 570 °C. The CB-Br sample had a weight loss region between 200 and 400 °C, and had 33.0% weight loss below 570 °C. The calculated amount of the ATRP initiator from the difference in weight loss between CB-Br and CB-COOH samples was 15.2%, which corresponds to 0.79 mmol g^{-1} , which is in acceptable agreement with the value measured by elemental analysis. The TEM images of the pristine carbon black in Fig. 2a and b show the typical structure of carbon black with the smallest structural unit having a diameter of tens of nanometers, with many aggregates (from several tens to several hundreds of nanometers), and some agglomerates larger than $1 \mu m$.

It is worth noting that an alternative way to synthesize CB-Br from CB-COCl can be used. In this procedure, ethylene glycol is first reacted with the CB-COCl to introduce the hydroxyl groups to the surface, and then 2-bromopropionyl bromide is added to introduce the initiator groups onto the carbon black surfaces by acylation. This method has been used for the functionalization of CNTs.³² However, some coupling may occur between different carbon black particles during the reaction of ethylene glycol with CB-COCl, which could be more significant than that observed for the CNT case, due to the close packing of the neighboring spherical particles in contrast to the loosely packed cylindrical tubes. Therefore, in order to avoid the potential



Fig. 1 TGA curves of CB, CB-COOH, and CB-Br.



Fig. 2 TEM images of crude carbon black (a and b) and CB-Br (c and d)

coupling between particles, ethylene glycol was first reacted with 2-bromopropionyl bromide to produce HEBiB, which was then added to CB-COCl.

Similarly, a compound containing both the azido group and the bromine group, 1-(azidomethyl)-4-(1-bromoethyl)benzene (AMBEB) was synthesized from CMS (Scheme 1b) to prepare



Scheme 1 Functionalization of carbon black with ATRP initiator by acid oxidation method (a) and nitrene chemistry method (b).

ATRP initiator modified carbon black by nitrene chemistry (CB-N-Br). This compound does not contain an ester bond, which should increase its stability under basic conditions compared to ATRP initiators tethered to the carbon black surface by ester bonds.³⁰ AMBEB was used as an initiator for the polymerization of styrene, demonstrating its feasibility in ATRP (Fig. S1 and S2†).

The surface of carbon black was modified with ATRP initiators by mixing CB with AMBEB in DMF and heated to 160 °C. The azide groups decomposed at high temperature to generate the highly reactive nitrene radicals that can covalently bond to the carbon surfaces via the [2 + 1] cycloaddition of nitrenes to the π -electron systems,³³ generating the nitrene modified carbon black (CB-N-Br). The Br content in the CB-N-Br was 1.84 mmol g^{-1} as determined by elemental analysis. This value is nearly three times larger than that of CB-Br (0.63 mmol g^{-1}) prepared by acylation of carboxyl group modified carbon black, which shows the higher grafting efficiency of the nitrene method. The TGA curves in Fig. 3 show that the CB-N-Br sample had a weight loss of 33.9% below 570 °C. The amount of ATRP initiator was 32.2%, determined from the weight loss difference between CB-N-Br and CB, which corresponds to ca. 1.52 mmol g^{-1} , in acceptable agreement with the value measured by elemental analysis. The morphology of CB-N-Br, as shown in the TEM images in Fig. 4, was similar to that of pristine carbon black, and the dispersibility of CB-N-Br was much better than crude CB, since it could be easily dispersed



Fig. 3 TGA curves of CB and CB-N-Br.



Fig. 4 TEM images of CB-N-Br.



Fig. 5 Photographs of CB-N-Br dispersion in different solvents after sonication. From left to right: THF, DMF, anisole, methanol, and water.

in THF, DMF, anisole, methanol, and water with ultrasonication (Fig. 5).

2 Grafting hyperbranched polymers from carbon black surfaces

2.1 Direct grafting of hyperbranched polymers. Hyperbranched or highly branched polymers have a three-dimensional dendritic architecture that creates potential applications in various areas due to their unique structural, chemical and physical properties.³⁴ As a synthetic method for hyperbranched polymers, the self-condensing vinyl polymerization (SCVP) of AB* inimer bearing both the vinyl group (A) and the initiating group (B*) was first exemplified *via* a cationic polymerization of 3-(1-chloroethyl)-ethenylbenzene.³⁵ SCVP of AB* inimer has also been performed by ATRP with *p*-chloromethylstyrene (CMS)³⁶ for the synthesis of hyperbranched homopolymers³⁷ or copolymers with styrene,³⁸ pentafluorostyrene,³⁹ *N*-cyclohexylmaleimide,⁴⁰ and chlorotrifluoroethylene.⁴¹

In this study, hyperbranched poly(*p*-chloromethylstyrene) (PCMS) was grafted from carbon black surfaces by SC-ATRP of CMS (Scheme 2). The polymerization of CMS was conducted with a CuCl/CCl₂/PMDETA catalytic system in the presence of carbon black modified with ATRP initiator. DMF was used as the solvent in order to improve the dispersibility of carbon black. NMR was used to determine the conversion of the CMS by measuring the decrease of the vinyl signal relative to the DMF peak as the internal standard (Fig. S3[†]). Fig. 6a illustrates that there was a nearly linear kinetics in the semilogarithmic plot. Nevertheless, some factors may influence the polymerization process: the initiators are immobilized on the surfaces, thus the chance of radical coupling between neighboring growing chains is increased; some of the initiator sites may not be accessible to the catalyst/ligand due to the steric hindrance in the agglomerated carbon black particles. During polymerization, the propagating polymeric radicals could be trapped by the polycondensed aromatic rings, and the quinonic and phenolic oxygens on carbon black.8 In addition, since the inimer, CMS, can initiate polymerization, some unattached polymers could also be formed in solution.

In order to determine the amount of the free (unattached) polymers in solution, samples were drawn from the reaction solution, with one part of the sample directly dried under vacuum to remove the solvent and monomer, and the residual solid was measured by TGA to obtain the value for weight loss, which corresponds to the total amount of the free and grafted



Fig. 6 (a) The plot of $In([M]_0/[M])$ and conversion vs. time, (b) GPC traces of free polymer in the reaction solution of CB-g-PCMS, and (c) TGA curves of CB-Br (1), CB-g-PCMS after (2) and before (3) washing with THF for $[CB-Br]_0/[CMC]_0/[CuCl]_0/[PMDETA]_0 = 1/400/0.95/0.05/1$, DMF/CMS = 1/2 (v/v), 100 °C. (d) TEM image of CB-g-PCMS.

polymer present in the composite. The other part was washed thoroughly with THF and separated by high-speed centrifugation until there was no free polymer detected in the upper solution by gel permeation chromatography (GPC) (Fig. S5⁺), and the separated solid was dried under vacuum and measured by TGA to obtain the weight loss of the grafted polymer. The TGA results (Fig. 6c) showed that the weight losses of CB-g-PCMS before and after washing were 60.1% and 42.1%, respectively. The content of the polymers on CB-g-PCMS was 53.0 wt%, after deducting the initial weight loss of CB-Br of 33.0%. The ratio of free polymer to the grafted polymer was estimated to be 3.3/1 (w/w) from the weight losses. The free polymer was also characterized by GPC. The samples were drawn from the reaction solution and the carbon black in the solution was separated by high-speed centrifugation. The polymers in the supernatant were characterized by GPC using linear polystyrene standards and the results are shown in Fig. 6b. The results show that the apparent molecular weights increased with reaction time with high dispersity (M_w/M_n) values in the range of 2.0-2.6, resulting from the hyperbranched nature of the polymers synthesized by SCVP. The peaks of oligomers were initially observed in the polymerization process, but their intensities gradually decreased compared to those of higher molecular weight polymer as conversion increased.

The morphology of the samples was studied by TEM. The carbon blacks grafted with hyperbranched polymers showed better dispersibility and more single particles in the TEM image (Fig. 6d), although there were still aggregates. A polymer layer can be observed on the carbon black surfaces, revealing the effective surface functionalization by controlled grafting of



Scheme 2 Grafting of hyperbranched PCMS from bromine group modified carbon black.

polymer. If the ATRP initiator is attached by the acid oxidation method, the resulting material is not suitable for the CO_2 capture applications, since the ester bonds on the surface can be hydrolyzed in the presence of KOH solutions. Therefore, the ATRP initiator modified carbon black prepared by the nitrene chemistry method is preferred for such CO_2 adsorption/desorption applications, since there are no ester bonds linking it to the surface, making it stable under strongly basic conditions.

Therefore, SC-ATRP of CMS was also conducted in the presence of CB-N-Br using the same reaction conditions. The conversion of the CMS was measured (Fig. S4[†]) and the semilogarithmic plot showed a nearly linear dependence on time (Fig. 7a). The apparent molecular weights increased with reaction time and then decreased, and the M_w/M_n values of the free polymers were all near 2 (Fig. 7b and Table 1), which was due to the continuous generation of new polymer chains initiated by



Fig. 7 (a) The plot of $\ln([M]_0/[M])$ and conversion vs. time, (b) GPC traces, (c) TGA curves of CB-N-g-PCMS at different polymerization time, and (d) the plot of $\Phi_{polymer}$ vs. conversion for $[CB-N-Br]_0/[CMS]_0/[CuCl]_0/[PMDETA]_0 = 1/400/0.95/0.05/1$, DMF/CMS = 1/2 (v/v), 100 °C. (e) TEM image of CB-N-g-PCMS.

Table 1 Data obtained from GPC and GPC-MALLS measurements of hyperbranched polymers formed at different polymerization time, and TGA measurements of CB-N-g-PCMS. [CB-N-Br]₀/[CMC]₀/[CuCl]₀/[PMDETA]₀ = 1/400/0.95/0.05/1, DMF/CMS = 1/2 (v/v), 100 °C

Entry	Time (h)	Conv. ^a	$M_{ m n,GPC}^{\ \ b}$	$M_{\rm w,GPC}^{c}$	$M_{\rm w,GPC}/M_{ m n,GPC}$	$M_{ m w,MALLS}^{d}$	$M_{ m w,MALLS}/M_{ m w,GPC}$	$f_{ m w}{}^e$	$\Phi_{ m polymer}{}^f$
1	4	1.4%	1810	3840	2.12	8720	2.3	0.574	0.132
2	12	7.1%	2600	5230	2.01	35 800	6.9	0.560	0.153
3	24	15.8%	3260	6720	2.06	40 600	6.0	0.534	0.192
4	48	34.5%	3010	6500	2.16	35 400	5.4	0.482	0.271
5	72	43.6%	2610	5380	2.06	35 600	6.6	0.455	0.312
6	96	48.6%	2200	4310	1.96	23 800	5.5	0.343	0.481

^{*a*} The conversion of the CMS in the polymerization measured by NMR. ^{*b*} Number-average molecular weight determined by GPC analysis in THF with linear polystyrene as the standard. ^{*c*} Weight-average molecular weight determined by GPC analysis in THF with linear polystyrene as the standard. ^{*d*} Weight-average molecular weight determined by GPC-MALLS. ^{*e*} The weight loss of the polymer-grafted carbon black samples measured by TGA. ^{*f*} The fraction of the polymers to the carbon black in the polymer-grafted carbon black samples.

benzyl chloride groups and thermal self-initiation of CMS.⁴² Gel permeation chromatography coupled with a multi angle laser light scattering detector (GPC-MALLS) was used to determine the absolute molecular weight of the hyperbranched PCMS. Because hyperbranched polymers have a smaller hydrodynamic volume than their linear counterparts with the same molecular weight, this leads to longer retention time in GPC and smaller apparent molecular weight measured by GPC.⁴³ The weight-average molecular weight values obtained by light scattering ($M_{w,MALLS}$) were larger than those obtained by standard GPC analysis by a factor of 2.3–6.9 (Table 1), confirming the existence of branched polymers.⁴⁴

The samples of CB-N-g-PCMS taken from the reaction solution were also washed thoroughly with THF and measured by TGA (Fig. 7c). As shown in Table 1, the weight losses increased gradually with polymerization time. The fraction of the polymers attached to the carbon black ($\Phi_{polymer}$) were calculated based on the weight losses. Fig. 7d shows that $\Phi_{polymer}$ increased linearly with conversion until 72 h and a sharp increase at 96 h, demonstrating that the amount of grafted

polymer increased as the polymerization progressed. This sharp increase in the $\Phi_{polymer}$ could be due to the increase in the number of benzyl chloride groups on the surface at higher conversion, which increases the likelihood of both monomers and polymers growing from this surface.⁴⁵ The TEM image (Fig. 7e) of CB-N-g-PCMS at 96 h showed the presence of polymers grafted around carbon black particles, and the free polymers seen as grey dots on the grid.

The degree of branching (DB) is an important parameter that characterizes the molecular structure of hyperbranched polymers.^{36d,46} In order to obtain the DB value of a polymer, nuclear magnetic resonance (NMR) is commonly used to quantify the peaks characteristic for different structures. However, PCMS does not show appropriate signal integrals when using CDCl₃ in the ¹H NMR spectrum due to the signal overlap. This issue was recently resolved by Komber *et al.* based on the aromatic solvent induced shifts (ASIS) effect.⁴⁷ When measuring the hyperbranched polymers with C₆D₆ and CD₂Cl₂ as the solvent by ¹H NMR, respectively, the corresponding characterized proton regions show sufficient signal separation. The signal integration

of the terminal (T), vinyl-type linear (L_V), condensation-type linear (L_C), and dendritic (D) units can be obtained. Therefore, DB can be calculated based on the following equation:⁴⁸

$$DB = 2I(D)/(2I(D) + I(L_V) + I(L_C))$$
(1)

For a linear polymer, DB = 0; for a perfect dendrimer, $DB = 1.^{36\alpha}$ The polymers formed in the sample of CB-N-g-PCMS at 96 h have 23.3% T units, 23.3% D units, 40.0% L_C units, and 13.5% L_V units, and a DB of 0.43 (Fig. S6†), indicating a highly branched structure for PCMS. The DB is lower than those prepared by polycondensation of AB₂ monomers, due to the lower activity of the primary chloride groups compared to the secondary ones.^{34a} It should be noted that the free polymers were precipitated into methanol before the NMR measurement, which removed the low-molecular-weight fractions which have a larger amount of T units.^{47a}

Large-scale experiments were conducted using the same conditions to obtain sufficient amounts of samples for the measurement of the specific surface areas of the polymer-grafted carbon black. The polymerization was stopped at 56% monomer conversion. The resulting sample was washed thoroughly with THF and dried under vacuum before performing nitrogen adsorption measurements. The Brunauer-Emmett-Teller (BET) specific surface area of the CB-N-g-PCMS is 21 m² g^{-1} . The crude carbon black had a surface area of 223 m² g⁻¹, and the loss of surface area after the polymerization is mainly due to the grafted polymer partially filling the micro-/meso pores. The TGA result showed the grafted polymers account for 52.3 wt% of the total mass of the sample. This equals to 24.9 mg m^{-2} of the carbon black surfaces. Assuming the density of PCMS is the same as that for polystyrene, 1.05 cm³ g⁻¹, the average thickness of the grafted polymers on carbon black surfaces is about 23.7 nm.

2.2 One-pot two-step grafting of crosslinked hyperbranched polymers. As discussed previously, the ATRP initiator modified carbon black prepared by the acid oxidation method contains ester bonds, which are not stable under alkaline conditions. Therefore, crosslinking the polymer with divinylbenzene (DVB) reduces the probability of cleaving the polymers from the surface. However, since this process could lead to crosslinking between different carbon black particles, enhancing aggregation, the synthesis has to be carefully controlled to minimize the extent of inter-particle crosslinking.

A model reaction with only the crosslinker was conducted to investigate the crosslinking process. The crosslinked polymer shell was formed on the carbon black surfaces by polymerization of DVB from the bromine groups of CB-Br, as shown in



Scheme 3 Preparation of carbon black with divinylbenzene (DVB) crosslinked shells.



Fig. 8 Plot of $ln([M]_0/[M])$ and conversion vs. time. $[CB-Br]_0/[DVB]_0/[CuCl]_0/[CuCl]_0/[CuCl]_0/[PMDETA]_0 = 1/50/4/0.2/4.2, DMF/DVB = 4/0.22 (v/v), at 100 °C.$



Fig. 9 The evolution of morphology of carbon black with DVB crosslinked shells at different conversions and the corresponding TEM images: 5 h (a), 25 h (b), and 72 h (c).

Scheme 3. Fig. 8 shows a nearly linear kinetic curve for the entire polymerization. The change of the morphology of the materials at different reaction time, 5 h, 25 h, and 72 h, was observed by TEM (Fig. 9). The polymer layer was very thin at a conversion of 2.5%, and cannot be easily observed in the TEM images. When the conversion increased to 11.6%, the polymer layer became thicker, and could be clearly seen in the TEM images. When the conversion further increased to 23.9%, the polymer layer was very thick, and in some areas, the polymer layer even formed a continuous network.

After conducting this model reaction, the one-pot two-step method was used to graft crosslinked polymers from the surface of the carbon black (Scheme 4). The CB-Br was first reacted with DVB to form a crosslinked polymer shell, and then CMS was added to the same pot to continue this reaction, forming the







Fig. 10 TEM images of CB-g-DVB (a and b) and CB-g-xPCMS (c and d).

crosslinked hyperbranched polymers from carbon black. In the first step of this reaction, the conversion of DVB was stopped at 14.3%, which was high enough to form a crosslinked coating without significant inter-particle crosslinking, as observed in the TEM images of CB-g-DVB (Fig. 10a and b). In the second step, the reaction was stopped when the total conversion of CMS and DVB reached 40.5%, as shown in the kinetic plot (Fig. 11). The TEM images (Fig. 10c and d) of the resulting sample of CBg-xPCMS show that the polymer layer on the carbon black was very thick, and some small aggregates were formed by interparticle crosslinking of polymer shells of neighboring particles. The SEM images in Fig. 12 show that after drying, the carbon black particles aggregated to form a layer with rough and porous surfaces. The surfaces of CB-g-xPCMS were smoother than the CB-g-DVB surfaces, since the former has more grafted polymers that decreased the surface roughness of the carbon blacks. In one previous report, a similar strategy was successfully used for preparing core/shell Au nanoparticles through a



Fig. 11 Plot of ln([M]₀/[M]) and conversion vs. time for step two of the one-pot two-step method for the grafting of crosslinked polymers. $[CB-Br]_0/[DVB]_0/[CMCS]_0/[CuCl]_0/[CuCl_2]_0/[PMDETA]_0 = 1/50/400/4/0.2/4.2, DMF/DVB = 4/0.22 (v/v), 100 °C.$



Fig. 12 SEM images of CB-g-DVB (a) and CB-g-xPCMS (b).

one-pot synthesis, where the gold core was first protected with a crosslinked polymer shell of ethylene glycol dimethacrylate (EGDMA), and then linear polymer brushes of poly(*n*-butyl acrylate) were grafted from the shell.⁴⁹

3 Functionalized carbon black for CO₂ capture

3.1 Introduction of quaternary ammonium hydroxide groups onto functionalized carbon black surfaces. The benzyl chloride groups in the hyperbranched PCMS were transformed into quaternary ammonium hydroxide groups, which allowed

Scheme 5 Synthetic procedures for the quaternization and ion-exchange reactions.



Fig. 13 TEM images of CB-N-g-PCMS-OH⁻ (a) and CB-N-Br-OH (b).

the material to be used for CO_2 capture by the humidity swing. The CB-N-g-PCMS was first quaternized using trimethylamine in ethanol and then ion-exchanged with KOH in methanol (Scheme 5). The elemental analysis showed that the Cl content was 13.28% for CB-N-g-PCMS, and it decreased to 1.24% after quaternization and ion-exchange over a one day period. Extension of the ion exchange process to 7 days decreased the Cl content to 1.11%, indicating that the one day ion-exchange procedure was sufficient.

A control sample with no polymer grafting (CB-N-Br-OH) was prepared using CB-N-Br as the feed by the same treatment (first with trimethylamine, followed by KOH). The TEM images of the two samples with or without grafting of polymers (Fig. 13) show different morphologies. For CB-N-Br-OH, no grafted polymer layer was observed on the particle surfaces, and there were more aggregates, which appear as dark agglomerates in the TEM images. However, for CB-N-g-PCMS-OH⁻, the polymer layer can be easily observed on the particle surfaces, which caused most of the particles to be separated from each other, leading to fewer and smaller aggregates. Also, the dispersibility of the functionalized carbon black improved due to the presence of grafted polymer layer.

The morphologies of the samples were also characterized by SEM. As shown in Fig. 14a and b, the pristine carbon black aggregated, while the smaller single particles (several tens of nanometers) are difficult to discern due to the limited resolution of SEM. The surface structure can be clearly observed for CB-N-Br-OH sample (Fig. 14e and f). The surface structure become blurred and cannot be easily observed for CB-N-g-PCMS-OHsample, due to the presence of polymer layers on the surfaces (Fig. 14c and d). In order to conduct SEM measurement for these samples, they were coated with a thin conducting layer by sputtering with Au to minimize the charging effects. In comparison, the same samples without Au coating were also characterized by SEM (Fig. S7 and S8[†]), which showed that for CB-N-Br-OH, the SEM images were nearly the same as that with Au coating because carbon black without polymer grafting has sufficiently high electrical conductivity; whereas for CB-N-g-PCMS-OH⁻, it became clear and there was less charging effects after Au coating due to the enhancement of conductivity.

3.2 CO₂ **capture results.** The CO₂ absorption/desorption characteristics of these materials are shown in Table 2 and Fig. 15. The material was first saturated with CO₂, before being exposed to humid conditions to release the CO₂ from the material in a closed system, followed by a reduction in the humidity to trigger the capture of the CO₂. In all cases a low humidity of approximately 5 parts per thousand (ppt) and a high humidity of approximately 20 ppt was used, which corresponds to approximately 20% and 90% relative humidity, respectively.^{25c} Excellion membrane, a commercially available extruded polyethylene membrane containing crosslinked chloromethylated polystyrene resin with quaternary ammonium hydroxide groups,^{25a,c} was selected as the reference material. When subject to the humidity swing, the Excellion membrane showed a swing size of 1.3×10^{-1} mmol g⁻¹, an



Fig. 14 SEM images of crude carbon black (a and b), CB-N-g-PCMS-OH⁻ (c and d), and CB-N-Br-OH (e and f).

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 Table 2
 The CO₂ capture results of Excellion membrane and carbon black samples. The overall rate is determined by: $\frac{1}{\text{overall rate}}$
absorption rate desorption rate

Entry	Material	Swing size (mmol g ⁻¹)	Absorption rate $(mmol g^{-1} min)$	Desorption rate $(\text{mmol } \text{g}^{-1} \text{min}^{-1})$	Overall rate (mmol g ⁻¹ min ⁻¹)
1 (ref. 25 <i>c</i>)	Excellion membrane	$1.3 imes 10^{-1}$	$4.0 imes10^{-3}$	$4.5 imes10^{-3}$	$2.1 imes 10^{-3}$
2	CB	0	0	0	0
3	CB-N-Br-OH	0	0	0	0
4 (ref. 25c)	CB-N-g-PCMS-OH	$1.4 imes 10^{-1}$	$1.8 imes 10^{-2}$	$1.2 imes 10^{-2}$	$7.2 imes10^{-3}$
5	CB-g-xPCMS-OH ⁻	$1.4 imes10^{-1}$	$2.0 imes10^{-2}$	$1.5 imes10^{-2}$	$\textbf{8.6}\times \textbf{10}^{-3}$



Fig. 15 Absorption/desorption profiles for Excellion membrane (a), CB-N-q-PCMS-OH⁻ (b), and CB-q-xPCMS-OH⁻ (c).

absorption rate of 4.0 \times 10⁻³ mmol g⁻¹ min⁻¹, a desorption rate of 4.5 \times 10⁻³ mmol g⁻¹ min⁻¹, and an overall rate of 2.1 \times 10^{-3} mmol g⁻¹ min⁻¹. The reversibility of the CO₂ absorption/ desorption based on the interchange of quaternary ammonium carbonate and bicarbonate groups under humidity swing has been demonstrated previously.25c,d

When the polymer-grafted carbon black, CB-g-xPCMS-OH⁻, was subjected to the humidity swing, there were marked improvements in the kinetics. As shown in the absorption and desorption traces in Fig. 15, it displayed an absorption rate of 2.0×10^{-2} mmol g⁻¹ min^{-1} , a desorption rate of $1.5\times10^{-2}\,mmol\,g^{-1}\,min^{-1}$, an overall rate of 8.6 \times 10⁻³ mmol g⁻¹ min⁻¹, and a swing size of 1.4 \times 10⁻¹ mmol g^{-1} . This carbon black sample with polymer grafting has nearly the same swing size as the Excellion membrane but a 3-fold increase in the absorption/desorption rates. In contrast, the crude carbon black and CB-N-Br-OH without polymer grafting showed no absorption/desorption when subjected to the humidity swing, since they contain nearly no quaternary ammonium hydroxide groups. Thus, the polymer grafting is vital for enhancing CO₂ capture because the polymer layer on the carbon black can greatly increase the number of accessible hydroxide groups and enhance the dispersibility of carbon black in solvents. Moreover, the CO₂ capture results for the CB-N-g-PCMS-OH- (ref. 25c) and CB-gxPCMS-OH⁻ samples have the same swing sizes $(1.4 \times 10^{-1} \text{ mmol})$ g^{-1}) and very close absorption/desorption rates (the overall rates are 7.2 \times 10^{-3} and 8.6 \times 10^{-3} mmol g $^{-1}$ min $^{-1}$, respectively). This implies that forming a crosslinked shell on carbon black has minimal influence on the swing size but can induce a slight increase of the CO2 absorption/desorption rates.

Conclusions

Carbon black with tethered hyperbranched polymers were prepared by surface initiated self-condensing ATRP. The ATRP initiator was introduced onto the carbon black surfaces by acid

oxidation followed by esterification, or by reaction of azide functionalized ATRP initiators with the carbon black surface using nitrene chemistry. ATRP was then conducted using a CMS inimer and CuCl/CuCl₂/PMDETA catalytic system in DMF at 100 °C. To maximize the stability of the polymer grafted carbon black under basic conditions, the nitrene chemistry approach is preferred to the acid oxidation method. Crosslinked hyperbranched polymers can be grafted from the carbon black as an alternative method for synthesizing functionalized surfaces that are stable under basic conditions. These crosslinked materials can be prepared in a one-pot two-step method, where the crosslinked shell was first formed on carbon black using DVB, followed by the polymerization of CMS to form a crosslinked hyperbranched outer layer. The morphologies of all the hyperbranched PCMS grafted carbon blacks were characterized by TEM and SEM, which confirmed the formation of the functional polymer layer on carbon black. TGA results revealed that the ratio of the grafted polymers to carbon black increased with polymerization time. The untethered hyperbranched polymers formed in the polymerization solution were characterized by ¹H NMR spectroscopy, GPC, and GPC-MALLS. The hyperbranched polymers on the carbon black surfaces were subsequently quaternized and ion-exchanged to generate quaternary ammonium hydroxide groups, which were utilized for the reversible capture and release of CO2 from ambient air. The crosslinked and uncrosslinked carbon blacks grafted with polymeric quaternary ammonium hydroxide groups showed a 3- to 4-fold increasing of the absorption/desorption kinetics compared with the Excellion membrane.

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