Electronic Supplementary Information

Effect of spray-drying and cryo-milling on the CO_2 absorption performance of polyethyleneimine-functionalized C_{60}

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Spray-drying

The components of the spray-drying equipment are shown in Fig. S1. The air brush (a) had a nozzle with a diameter of 0.3 mm and a dual action trigger that allowed controlling both PEI/C_{60} solution and N_2 flows. All spray-dried samples were prepared with solution and N_2 fully open flows. The N_2 pressure was set in the range of 10-60 psi using a gas cylinder regulator. The two-stage oven (b) was a Nanotech Innovations SSP-354 with two temperature-controlled sections. The temperature of the first section was set between T_1 = 250-310 °C for a fast evaporation of the solvents, followed by a second section at T_2 = 100 °C to fully dry the product. The collecting unit (c) was composed of a metal mesh (50 US Mesh), an o-ring, and a two-part enclosure with a sealing clamp. The spray-dried PEI-C_{60} was collected on the metal mesh as brown powder (d), the powder was removed in ethanol using bath sonication, filter on a 0.45 pore μm PTFE membrane and let dry.

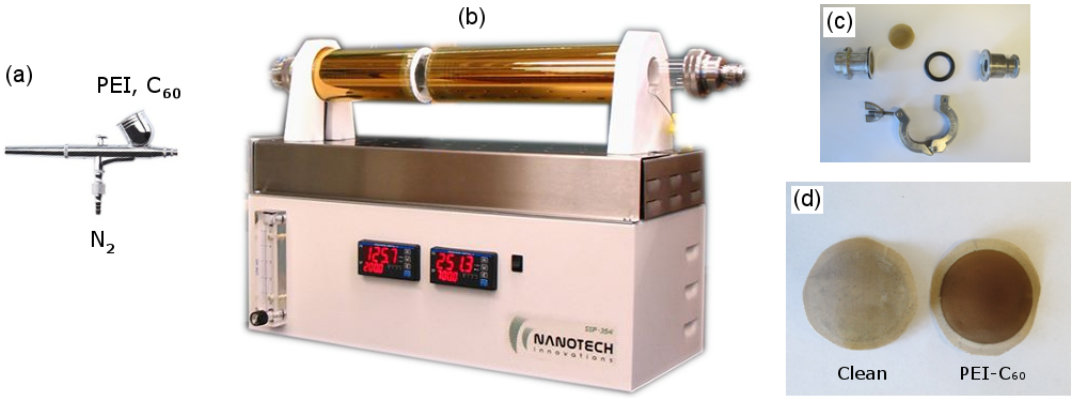

Figure S1 Components of the spray-drying equipment.

The experimental conditions used in the preparation with the absorption performance and characteristics of the spray-dried products are summarized in Table S1.

Figure S1 Preparation, characteristics and wet CO_2 absorption performance of the spray-dried PEI-C_{60} products.

Sample #	C_{60} (mg) / Toluene (mL)	PEI (mg) / $CHCl_3$ (mL)	T_1 (°C)	T_2 (°C)	$P(N_2)$ (psi)	$CO_2 + H_2O$ Uptake (wt%)		Aspect
						@ 90 °C	from 90 °C to 25 °C	
1	10 / 5	25 / 5	280	100	60	12.1	12.3	Fine powder
2	10 / 5	50 / 5	280	100	60	12.3	14.7	Fine powder
3	10 / 5	75 / 5	280	100	60	2.6	8.5	Clusters
4	10 / 5	100 / 5	280	100	60	-	-	Sticky
5	10 / 5	50 / 5	250	100	60	-	-	Sticky
6	10 / 5	50 / 5	310	100	60	12.7	18.2	Very fine powder
7	10 / 5	50 / 5	310	100	10	8.2	12.7	Sticky
8	10 / 5	50 / 5	280	100	10	13.9	13.1	Fine powder
9	10 / 5	50 / 5	280	100	5	11.5	12.7	Powder
10	5 / 5	25 / 5	280	100	10	14.2	12.0	Very fine powder
11	5 / 5	25 / 5	310	100	10	11.4	8.0	Fine powder
12	7.5 / 5	37.5 / 5	310	100	10	14.0	12.0	Fine powder
13	10 / 12	90 / 3	Ultrasonication			14.2	7.3	Clusters

Cryo-milling

The PEI-C_{60} cryo-ground samples were prepared as follows.

Ultrasonic synthesis (as prepared sample): In a glass vial, 10 mg of C_{60} were dissolved with 12 mL of toluene to which was added 0.5 mL of Et_3N. In another vial, 0.1 g of PEI was dissolved with 3 mL of $CHCl_3$. The PEI solution was added with a syringe to the C_{60} one drop-by-drop which was immersed in an ice-bath and probe-sonicated at 150 W. A brown precipitate of PEI-C_{60} was formed. This procedure was repeated as many times as necessary in order to collect enough material for the cryo-milling. Such material was then filtered, washed with $CHCl_3$ in excess, and let dry on a 0.45 μm pore PTFE filter. A reddish-brown rubbery and clustery material was collected.

Stir bar synthesis (as prepared sample): 0.5 g of C_{60} was dissolved in 600 mL of toluene in a 1 L round-bottomed flask to which 25 mL Et_3N and a magnetic stirring bar were also added. In a separate flask, 5.0 g of PEI was dissolved in 150 mL of $CHCl_3$. The PEI solution was transferred in the C_{60} flask using a 50 mL glass syringe kept vertical to allow free flowing by gravity while vigorously stirring. The PEI-C_{60} precipitated from the reaction mixture was filtered, washed with $CHCl_3$ in excess, and let dry on a 0.45 μm pore PTFE filter. A cake of brown hard material was collected.

Cryo-ground sample: PEI-C_{60} from the ultrasonic or stir bar synthesis was transferred to the grinding vial in which a stainless still impactor was previously placed. The material covered the impactor up to about 2/3 of its height. The vial was then loaded in the cryo-grinder filled with liquid nitrogen beforehand. The grinder was closed and the vial left immersed in liquid nitrogen for about 30-60 min. prior to the starting of the milling procedure. The procedure consisted in two parts: 1) 3 min. milling at 10 counts per second (CPS), and 2) 3 min. cooling to avoid heating the material, this cycle was repeated three times. The vial was then removed from the grinder and before opening it, allow to reach room temperature in order to avoid water condensation on the final product.

Dried and cryo-ground sample: PEI-C_{60} from the ultrasonic synthesis was placed to dry at 90 °C under N_2 flow. The dried material was then processed following the same procedure described for the cryo-grinded sample above.

The absorption performance of the cryo-milled products are summarized in Table S2.

Table S2 Wet CO_2 absorption performance of the cryo-milled PEI-C_{60} products.

Sample	**CO_2 + H_2O Uptake (wt%)**	
	@ 90 °C	**from 90 °C to 25 °C**
Ultrasonic synthesis	12.4	7.8
Stir bar synthesis	12.1	9.6
Ultrasonic + Cryo-grinding	13.4	6.2
Ultrasonic + Drying + Cryo-grinding	5.4	5.4
Stir bar + Cryo-grinding	11.0	17.6