Supporting Information

Rapid and continuous atmospheric plasma surface modification of PAN-based carbon fibers

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1. Plasma setup in this work

**Figure S1.** Photos of continuous and rapid atmospheric plasma equipment in this work: (a) Front view, (b) Rear view, (c) Side view.

The continuous and rapid atmospheric plasma equipment was designed for the surface modification of PAN-based carbon fibers, and the equipment photos were shown in Figure S1. The intensity of the plasma field was controlled by a SPA5000 power supply (not shown on the above figures).
2. XPS analysis

**Figure S2.** Surface C/N/O element intensity of plasma-treated CF: (a) untreated CF; (b) 7.5s plasma-treated CF; (c) 15s plasma-treated CF; (d) 30s plasma-treated CF; (e) 60s plasma-treated CFs.

XPS test was used to characterize the surface element content of plasma-treated carbon fibers, then O/C and N/C ratio could be obtained to indicate the effect of atmospheric plasma.
3. Raman spectrum

**Figure S3.** Raman peak fitting images of plasma-treated CFs with different time 0s(a), 7.5s(b), 15s(c), 30s(d), 60s(e).

Experimental Raman spectra were collected by using a Renishaw InVia Raman microscope, which equipped with a 514 nm Ar-ion laser, and the laser power was set to 10%. The laser lines
used graftings of 2400 l/mm. The analysis adopted five-peak model, which fitted the D1 (1350 cm⁻¹), G (1580-1600 cm⁻¹), D2 (1620 cm⁻¹), D3 (1500 cm⁻¹), and D4 (1180 cm⁻¹).

| Samples  | CF-0s | CF-7.5s | CF-15s | CF-30s | CF-60s |
|----------|-------|---------|--------|--------|--------|
| D1/G     | 2.05  | 3.25    | 4.38   | 4.06   | 3.99   |

Table S1. The D1/G ratios of plasma-treated CFs

4. Fibers diameter test

Figure S4. The frequency distribution histogram of CFs diameter (a) CF-0s, (b) CF-7.5s, (c) CF-15s, (d) CF-30s, (e) CF-60s.

In order to characterize the mechanical properties of fibers, the diameter of a hundred fibers is counted to calculate the mean diameter (d) of CFs by SEM images, the statistical result shows there is no effect on the diameter of CFs after atmospheric plasma treatment.
5. Tensile tests

Table S2. The tensile strength and tensile modulus of resin impregnated CF bundles

| Sample    | Tensile Strength/GPa | Elongation/% | Tensile modulus/GPa |
|-----------|----------------------|--------------|---------------------|
| Toray T300| 3.50                 | 1.51         | 231.78              |
| CF-0s     | 3.51                 | 1.52         | 230.92              |
| CF-60s    | 3.49                 | 1.49         | 234.22              |

The mechanical properties of carbon fiber tows were tested using INSTRON-5567 universal testing machine on the basis of ASTM D4018-17 standard.

6. Wettability test

Figure S5. The wettability of CFs with different plasma treatment time.

The wettability between CFs and water was analyzed by a multifunctional tensiometer (Krüss DSA30) using a pendent-drop method, where the evolution of water droplet with time was recorded after the water phase was slowly deposited onto the CFs surfaces. Carbon fiber tows were
evenly spread and placed on a flat stage. One water droplet was deposited by a syringe pointed vertically down onto the sample surface, and a high-resolution camera captures the image. The spreading of the droplet on CFs were observed by taking pictures incrementally. The spreading velocity of water droplets was used to characterize the influence of plasma on the hydrophilicity of fibers surfaces. It was worth to note that, due to the rough surface that composed of aligned fibers, the droplet would completely wetting the fiber substrate when the contact angle is lower than 90°. Thus, this method is a qualitative wettability test, the precision of contact angle is not comparable with that of single filament wettability test.

7. Cost estimation

Carbon Fibers surface treatment in the same laboratory was taken as an example to compare the time and cost of electrochemical anodization and plasma surface treatment. Their photos are shown in Figure S6.
**Figure S6.** The size comparison of plasma (a) and electrochemical oxidation (b) equipment in lab. Both equipment can process one tow of carbon fiber up to 24K in tow size.

For electrochemical anodization treatment, the CFs undergoes surface treatment, washing and drying steps and the costs mainly include energy consumption and the raw materials. The energy cost includes electricity for anodization process, thermal drying oven and water pump for washing. The raw material cost is mainly from ammonium bicarbonate electrolyte. The operation speed of carbon fiber is set to 16.8m/h, the total cost was listed in Table S3.

**Table S3.** The cost estimation of electrochemical oxidation and plasma treatment in lab.

|                         | Cost         | Step                     | Power/W | Time/s | Waste                          | Total               |
|-------------------------|--------------|--------------------------|---------|--------|--------------------------------|---------------------|
| **Electrochemical oxidation** |              | anodization process      | 230     | 214    |                                | 4.06~4.44$/per kilogram |
|                         |              | water pump               | 300     | 110    |                                |                     |
|                         |              | drying oven              | 3200    | 150    |                                |                     |
|                         | The raw material | Electrolyte             | Unit price/$ | 2.63 | 1.5                            |                     |
|                         |              | ammonium bicarbonate     |         |        | The waste of electrolyte and air pollution |                     |
| **Plasma treatment**    |              | Energy consumption       |         |        |                                | 1.52~1.67$/per kilogram |
|                         |              | air compression pump     | 800     | 60     | No                             |                     |
|                         |              | DBD plasma equipment     | 600     | 60     |                                |                     |

According to the table, it takes 7.9 minutes for electrochemical oxidation (including washing and drying) to process the same length of CFs, which is 7.9 times as much as plasma treatment. When the surface treatment of T-300 CFs is carried out by these two methods, the total cost of electrochemical oxidation is 4.06~4.44$ per kilogram, while the cost of plasma treatment is 1.52~1.67$ per kilogram in the lab. Besides, the cost of electrochemical treatment equipment is about 89500$, while the cost of plasma treatment equipment is 9140$. Therefore, plasma treatment has the advantages of high-efficiency, environmental-friendly, low cost and simplicity of operation, which is a promising candidate for the surface modification of CFs.
Figure S7. Carbon fiber production cost structure.

For the industrial production of carbon fibers, the composition of production costs is mainly divided into three categories, including direct costs, depreciation of fixed assets, and current costs, and each production cost structure is shown in Figure S7.

The "Action Plan for Accelerating the Development of the Carbon Fiber Industry" issued by the Ministry of Industry and Information Technology mentions that the carbon fibers industry has economies of scale, which means that the production costs can be greatly reduced by increasing the throughput of the production line. On the basis of not changing the production line on a large scale, the way to increase the output is to rise the speed of the production line. If the wire speed is doubled, the existing output can be increased to about 1.7 times the original, thus reduce the production cost of carbon fibers. However, it is difficult for traditional electrochemical treatment to match the increased processing speed due to the large size and complicity of the equipment. Compared with traditional electrochemical treatment, plasma treatment is compact and can be easily adjusted to match the line speed without significantly modifying the equipment and waste treatments, thus increasing the efficiency and lowering the cost of CF production line.

8. The preparation of ILSS test splines
The ILSS test splines were manufactured by compression molding technology, and the specific production process was shown in Figure S8.

(a) The molds required for the preparation of ILSS splines were shown in Figure S8(a).

(b) The carbon fibers were unidirectionally arranged on tailor-made mold.

(c) The test sample used epoxy resin E-44 as the matrix resin and triethylentetramine as the curing agent. The two were mixed in a ratio of 10:1, fully stirred and then quickly coated
on the surface of the carbon fibers. Glass rod was used to scrape off excess resin so that the resin and the fibers can be fully infiltrated as much as possible.

(d) Place the splines in a special mold.

(e) The two molds were combined to ensure adequate infiltration of resin and fibers, and the mold was set using a hydraulic press.

(f) Put the mold into the oven at 120 °C for 2 hours, so that the composite material was fully cured and formed, and the ILSS test splines were obtained after cutting.