

Supporting Information

**Reuse of Spent Industrial Graphite in Batteries by Green Recycling
and Interphase Functionalization**

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Experimental section

Material Preparation: The spent graphite powder (SG) was obtained through the following procedure. First, the commercial spent LIBs supplied by Changhong Sanjie New Energy Co., Ltd. were disassembled at full discharge and the graphite anode sheets were physically separated from the cathode sheets and separator. Then the graphite anode sheets were mechanically crushed into powders, which were next winnowed to separate the graphite and current collector Cu. The obtained SG powder was then treated with a low-concentration citric acid aqueous solution. Specifically, 10 g of SG was added into 50 g of 0.2 mol L⁻¹ citric acid solution, which was water-bath heated at 60 °C for 2 h. The suspension was filtered and washed with water until the filtrate was neutral. The obtained citric acid-treated graphite (AG) powder was next added into 0.2 wt% of gelatin aqueous solution. After being magnetically stirred for 30 min at 60 °C, the mixture solution was kept at rest for 10 min. During the rest, the graphite powder spontaneously settled down because of gravity. At last, the upper layer of the solution containing floating impurities was poured off and the remaining graphite precipitate was collected through water-washing, centrifuging and drying. The obtained purified graphite is denoted as PG.

For comparison, SG was also purified through a conventional route involving strong acid leaching and high-temperature calcination. Specifically, SG was first treated with 2 mol L⁻¹ hydrochloric acid solution at a liquid-solid ratio (L/S) of 5:1. The acid leaching temperature and time period are 60 °C and 2 h, respectively. After the filtration and water-washing, the obtained graphite was further calcined under nitrogen atmosphere at 900 °C for 5 h. The graphite recycled through this conventional method is denoted as CG.

Material characterization

Scanning electron microscopy (SEM) (Hitachi S-8010) and transmission electron microscopy (TEM) (FEI Tecnai HT7700, 120 kV) were employed to examine the morphology and microstructure of the graphite powder and cathode. The graphite samples for TEM testing were prepared through ultrasonic dispersion of graphite powder or cathode in anhydrous ethanol and subsequent drying on carbon films under

an infrared light for 30 min.

X-ray diffraction (XRD) (RINT 2000, Rigaku with Cu K α irradiation source) was used to characterize the crystalline structure of graphite powder and cathode. Thermogravimetry (TG) analysis was carried out in an STA 200 thermal analyzer (Hitachi STA 200). Raman spectra were acquired using a Jobin Yvon Lab HR 800 instrument with a 532 nm excitation laser. Fourier transform infrared (FTIR) spectroscopy (Bruker Optics, Tensor 27, Borken, Germany) was utilized to characterize the functional groups of graphite powder and cathode.

X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher, Waltham, MA, USA) was conducted on the cycled graphite cathode surface to investigate the composition of the graphite surface. After 500 cycles, the graphite cathodes were extracted from the cells, washed with solvent EMC and then vacuum dried for 12 hours to prevent potential oxidation or contamination by air during the XPS analyses. The morphology and Young's modulus of the cathode/electrolyte interphase were measured through atomic force microscopy (AFM) (Dimension Icon, Bruker, Germany).

Electrochemical characterization

Preparation of graphite cathode: To prepare the graphite cathode slurry, graphite, Super P, and polyvinylidene fluoride (PVDF) were mixed with a mass ratio of 8:1:1 and dispersed in N-methyl-2-pyrrolidone solvent (NMP). The slurry was stirred with a high-speed shearing machine for thirty minutes to ensure thorough mixing. The slurry was then uniformly coated on the surface of an aluminum foil current collector with a coating machine. The cathode sheets were pre-dried for 12 hours at 60 °C, and then cut into small discs with uniform diameter of 13 mm. Before the cell assembly, the graphite cathode discs were completely dried in a vacuum drying oven at 120 °C overnight. The loading of active graphite material was controlled at 2 ± 0.2 mg cm $^{-2}$.

Electrochemical measurements: The graphite cathodes were transferred into an argon-filled glove box for the assembly of CR2032 coin cells (water content < 0.1 ppm, oxygen content < 0.1 ppm). Li||graphite cells were assembled using Li discs as counter

electrodes. The electrolyte is 4 mol L⁻¹ of LiPF₆ dissolved in ethyl methyl carbonate solvent (EMC). Glass fiber filters (Whatman) with diameter of 19 mm were used as separators. The quantity of electrolyte for each cell was 150 uL. Charge and discharge tests were performed on a battery test system (LAND CT2001A) within a voltage range of 3.0-5.0 V. The galvanostatic intermittent titration technique (GITT) test was performed by repeatedly charging at 0.5 C for 90 seconds and resting for 180 seconds until the voltage reaches 5 V, and then discharging with the same procedure as during charging until the voltage reached 3 V. Electrochemical impedance spectra of the Li||graphite two-electrode cells were obtained using a Bio-Logic electrochemical workstation with a frequency range from 100 kHz to 0.1 Hz and an amplitude of 5 mV. Since the Li||graphite cells contain the same Li counter electrodes, the differences in the impedance spectra mainly originate from the graphite electrodes. So only the graphite electrodes are taken into consideration in the fitting procedure and equivalent circuit.

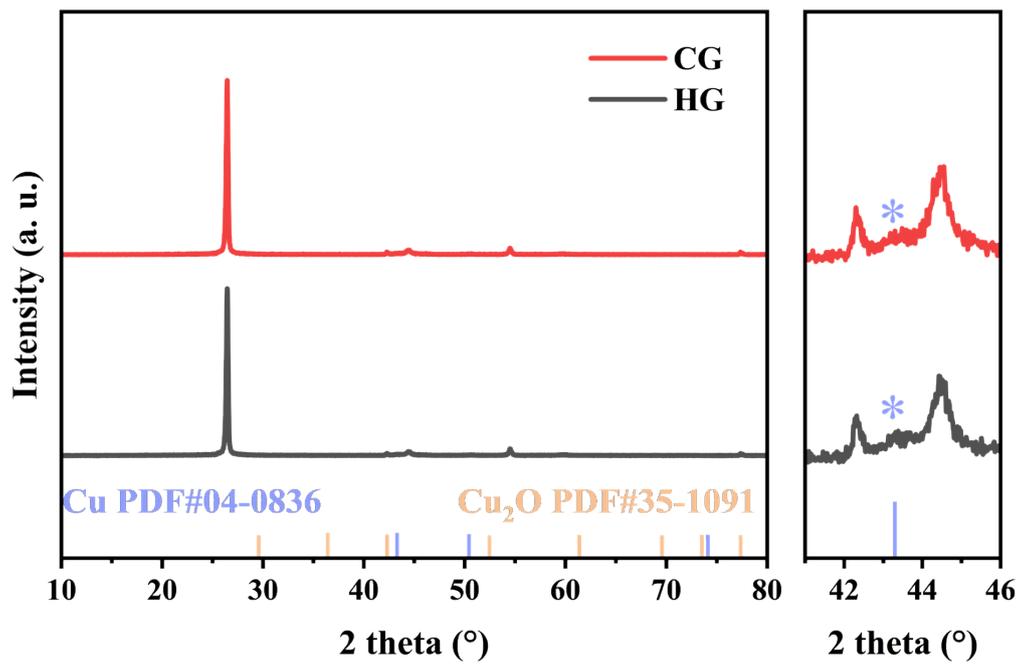


Figure S1. XRD patterns of HCl-treated graphite (HG) and CG.

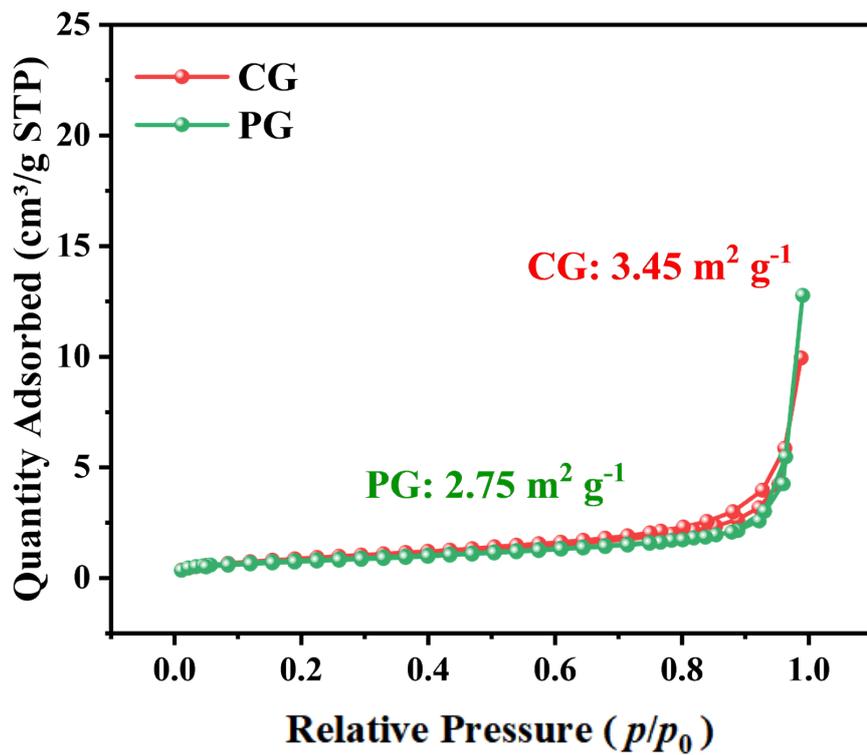


Figure S2. The nitrogen adsorption-desorption isotherms of CG and PG.

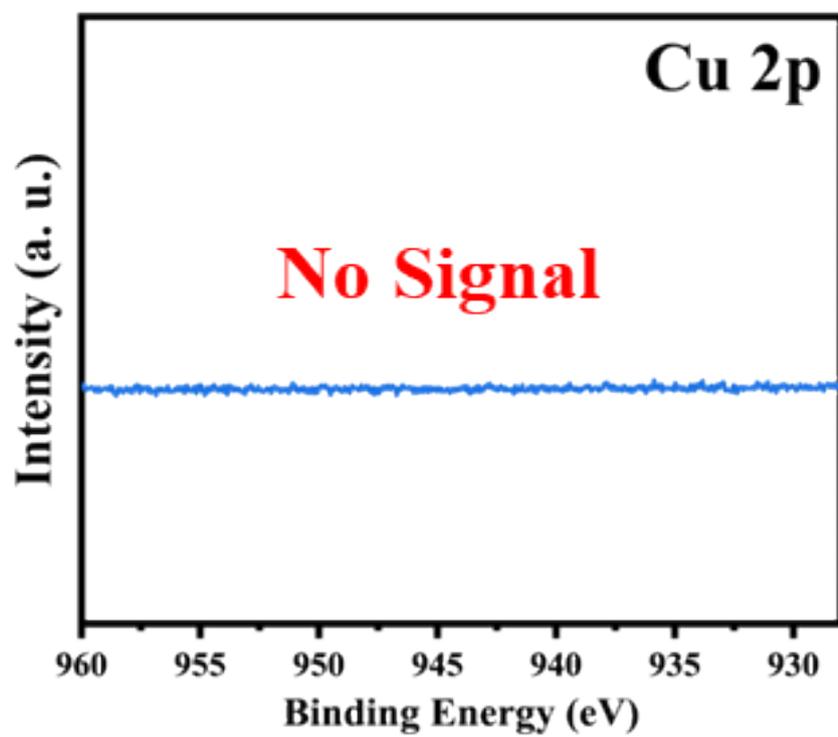


Figure S3. XPS spectrum of PG in the core-level region of Cu 2p.

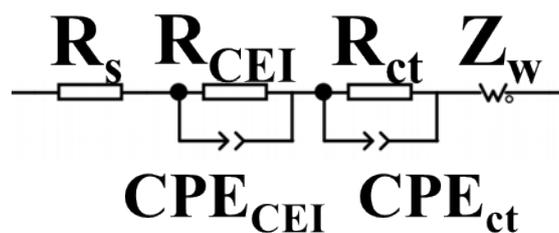


Figure S4. The equivalent circuit used for the fitting of Nyquist plots.

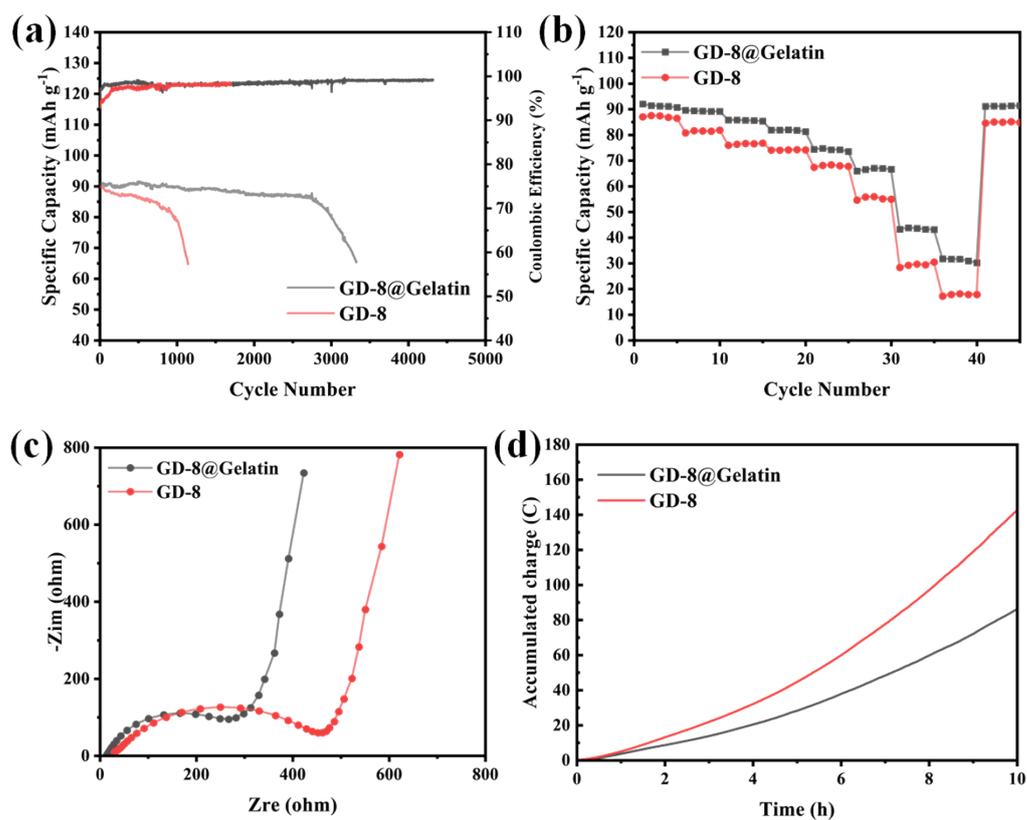


Figure S5. (a) The long-term charge/discharge performance, (b) rate behavior, (c) electrochemical impedance, (d) accumulated charges during the storage at 5.0 V of pure NG (GD-8) and gelatin-coated NG cathodes (GD-8@Gelatin).

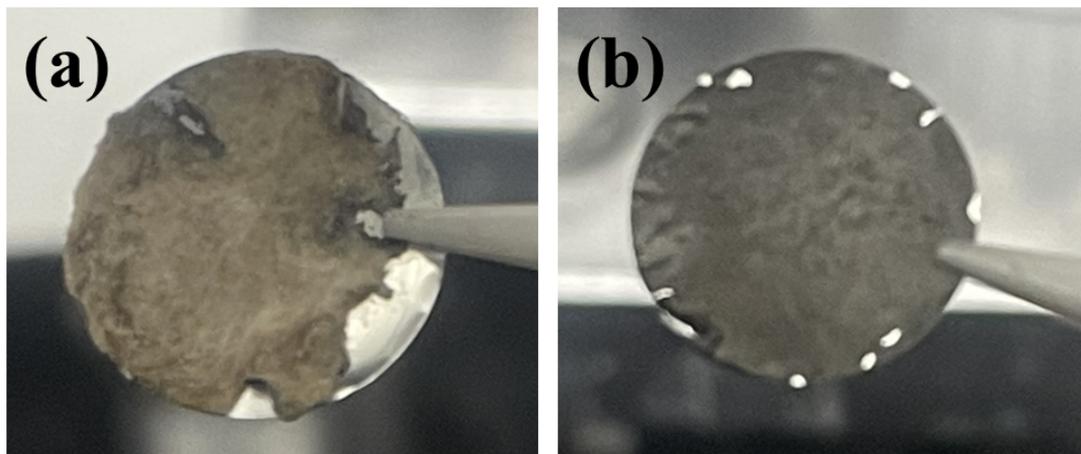


Figure S6. The optical photographs of (a) CG and (b) PG graphite cathodes taken out from the Li||graphite cells.

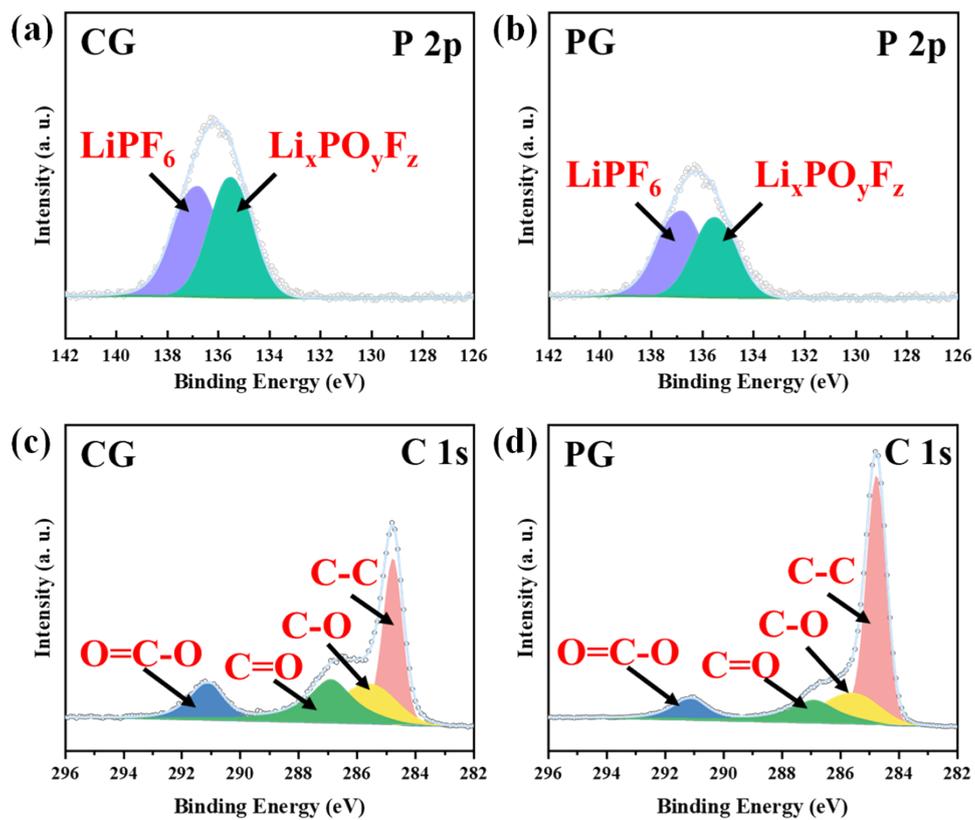


Figure S7. XPS of the CG and PG cathodes after long-term cycling in the core-level regions of P2p and C1s.

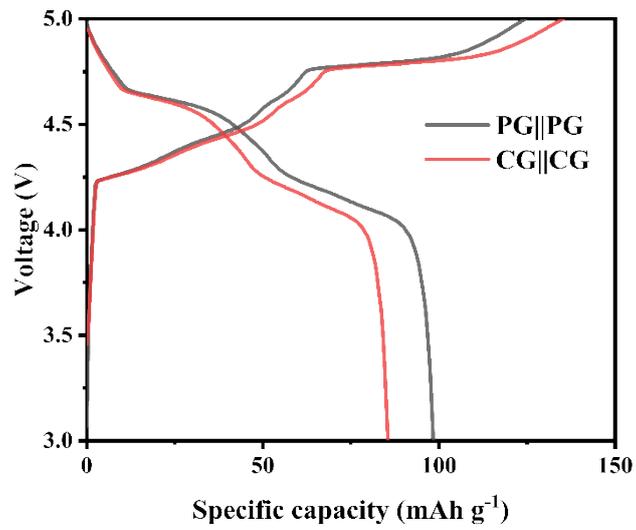


Figure S8. The charge/discharge curves of CG||CG and PG||PG dual-carbon DIBs.

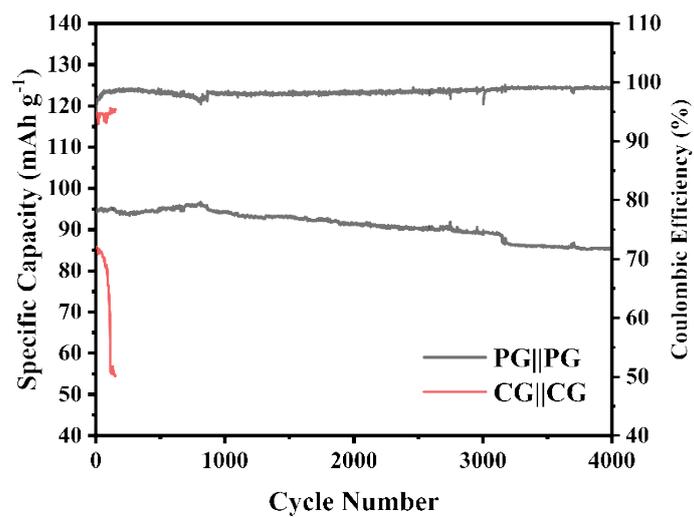


Figure S9. The long-term cycling capacity and coulombic efficiencies of CG||CG and PG||PG dual-carbon DIBs.

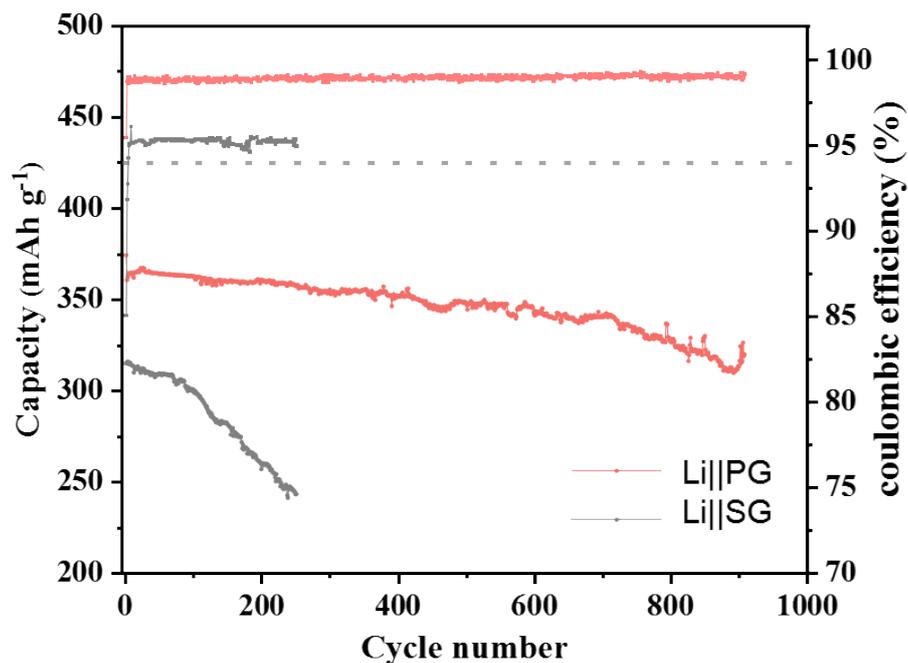


Figure S10 The long-term cycling capacity and coulombic efficiencies of Li||SG and Li||PG cells in the potential of range 2.0 V-0.01 V.

The electrochemical performance of PG and SG as the anode material of LIBs was measured in the potential of range 2.0 V-0.01 V vs. Li counter electrode. The specific capacity of PG during the initial cycle is around 362 mAh g⁻¹, which is significantly higher than that of SG. The capacity retention of Li||SG cell is 88% in the 900th cycle, while that of Li||PG cell is only 77% in the 250th cycle.

Table S1. The metal element contents (ppm) of different graphite materials.

	Cu	Ni	Co	Mn	Li
SG	65.19	2.955	1.44	1.144	0.629
CG	20.35	0.192	0.059	0.061	0.005
AG	0.313	0.261	0.015	0.055	0.006
PG	0.069	0.108	0.007	0.023	0.002

Table S2. The graphitization degree of different graphite powders.

The degree of graphitization	
SG	0.87
CG	0.85
AG	0.92
PG	0.94

The degree of graphitization (G) of carbon materials was typically calculated using X-ray diffraction (XRD) technology. By measuring the interlayer spacing d_{002} of the (002) plane of graphite, the Mering–Maire formula (also known as the Franklin formula) was applied to calculate the degree of graphitization. The specific calculation formula is as follows:

$$G = \left(\frac{0.3440 - d_{002}}{0.3440 - 0.3354} \right) * 100\%$$

where G represents the degree of graphitization expressed as a percentage, d_{002} is the interlayer spacing of the (002) plane of the carbon material with the unit in nanometers (nm), 0.3440 nm is the interlayer spacing of non-graphitized carbon, 0.3354 nm is the interlayer spacing of ideal graphite crystals.