Electronic Supplementary Material (ESI) for Chemical Communications.

Template free preparation of graphene tubes from polyimide catalyzed by calcium carbonate

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EXPERIMENT:

1. Chemical and reagents

Pyromellitic dianhydride (PMDA, 99%) and 4,4′ -oxydianiline (ODA, 99%) were purchased from Changzhou Sunlight Medical Raw Material Co., Ltd. N,N-dimethylacetamide (DMAc, ≥99.8%) and Calcium carbonate ($CaCO_3$,97%) were purchased from Shanghai Macklin Biochemical Co., Ltd.

2. Preparation of graphene tubes

Disperse the $CaCO_3$ in DMAc by ultrasound to prepare a catalysts dispersion ($CaCO_3$ and PAA mass ratio of 5 wt%). Firstly, dissolve ODA in DMAc, then add PMDA to the solution to prepare a PAA solution with a solid content of about 25wt%, and stir the solution for 3-4 hours until the reaction is complete. Then, add the catalysts dispersion into the PAA solution and continue stirring for 1 hour to fully disperse the $CaCO_3$, resulting in a final solid content of 22 wt% for PAA. Pour the final solution onto a clean glass plate, dry the solvent at 90 ^oC, and then maintain it at 250 ^oC and 350oC for 10 minutes respectively to obtain a PI/$CaCO_3$ composite film.

As shown in the **Figure S1**, sandwich the PI film between graphite molds, heat the composite film to 1500 ^oC under vacuum conditions at a heating rate of 2 ^oC/min and then cool it to room temperature, and take out the carbonized PI film. It can be visually observed that there are many colonies-like GTs distributed on the surface of the carbon film. The GTs on the carbon film can be collected by ultrasonic treatment in alcohol and filtration. To explore the formation conditions and mechanism of GTs, the same method was used to prepare PI/CaO composite films with CaO as the catalyst and perform simultaneous heat treatment. In addition, the PI/$CaCO_3$ film was heat-treated at the same temperature and heating rate under argon protection in a tube furnace.

3. Structure characterization

The X-ray diffraction (XRD) pattern were recorded using a D/MAX-Ultima IV X-Ray Diffractometer at room temperature (Cu Kα, 40 kV, 30 Ma). The interlayer spacing of the graphite was calculated by using the Bragg's equation as following:

$$\lambda=2d_{002}\cdot\sin\theta \quad \text{(ES1)}$$

where the λ is X-ray wavelength of Cu Kα (=0.154178 nm), θ Is the Bragg diffraction angle of

the GTs, and d_{002} is the d-spacing of the (002) plane.

Raman spectra were recorded using a LabRAM HR Evolution (HORIBA Jobin Yvon) with an excitation wavelength of 532 nm. SEM (SU8220, Hitachi) with an accelerating voltage of 15 kV. The SEM image and elemental mapping were obtained with a Hitachi SU8220 field emission scanning electron microscope. High resolution transmission electron microscopy (HRTEM) images of graphene tubes were collected with a Tecnai (G2 F20 S-TWIN) transmission electron microscope. The pyrolysis process of PI film was collected by thermogravimetric-mass spectrometry(Rigaku, thermo plus EV2/thermo mass photo) at Argon atmosphere. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific K-Alpha spectrometer.

Figure S1-S5 and Table S1

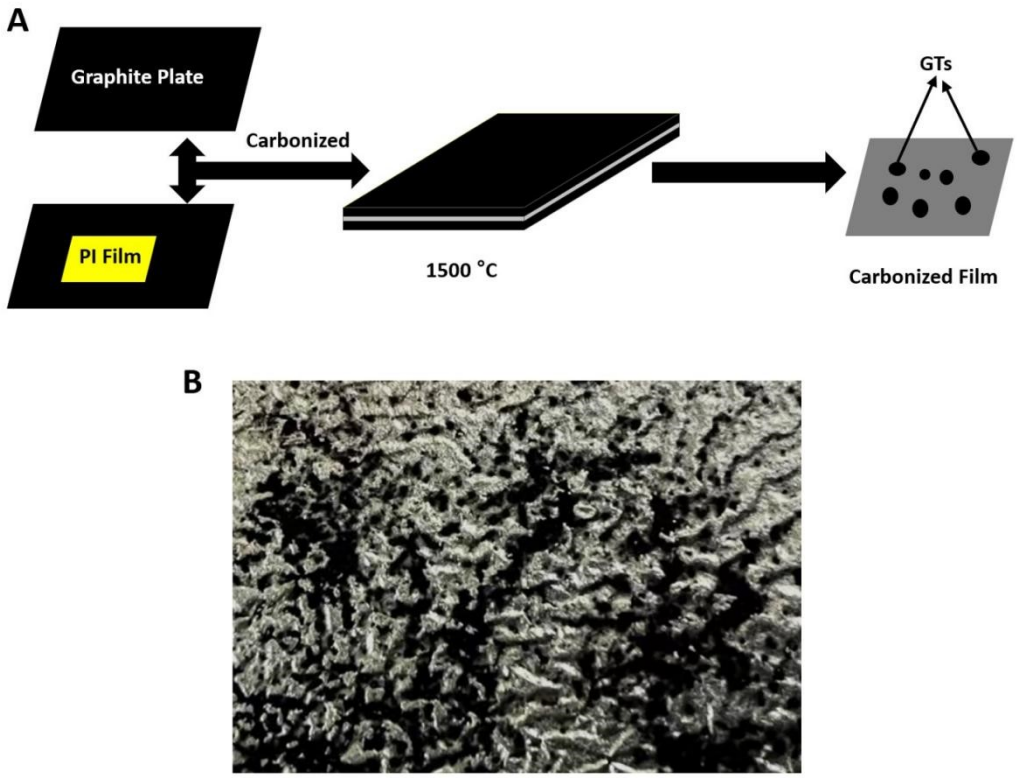

Figure S1. (**A**) Heat treatment process of polyimide film and schematic of how graphene tubes are distributed on carbon films, (**B**) The sample image.

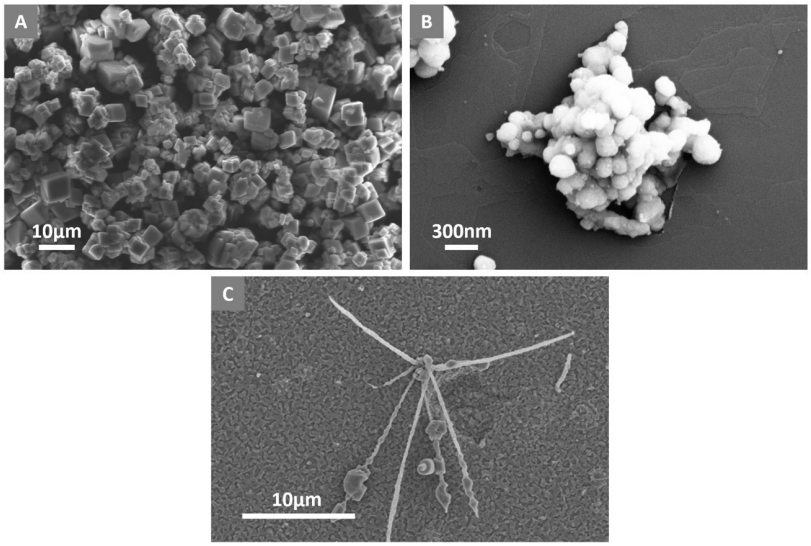

Figure S2. SEM image of (**A**) $CaCO_3$ and (**B**) CaO ($CaCO_3$ heat treatment after 900°C), (**C**) GTs grown in situ on PI/CaO carbon film.

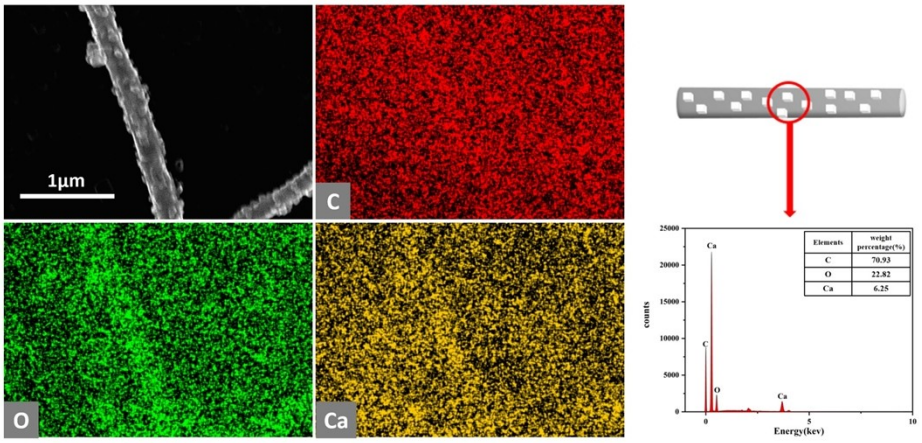

Figure S3. Element mapping of the CaO encapsulated graphene tubes which were prepared at 1200 °C. Due to the relatively high mole fraction of $CaCO_3$ initially doped in the PI film, a large amount of CO_2 gas was produced when the $CaCO_3$ decomposes, and the release of CO_2 molecules and their diffusion, deposition and collision drive these small CaO particles to attach on the tube walls, but the probability of this structure is extremely low.

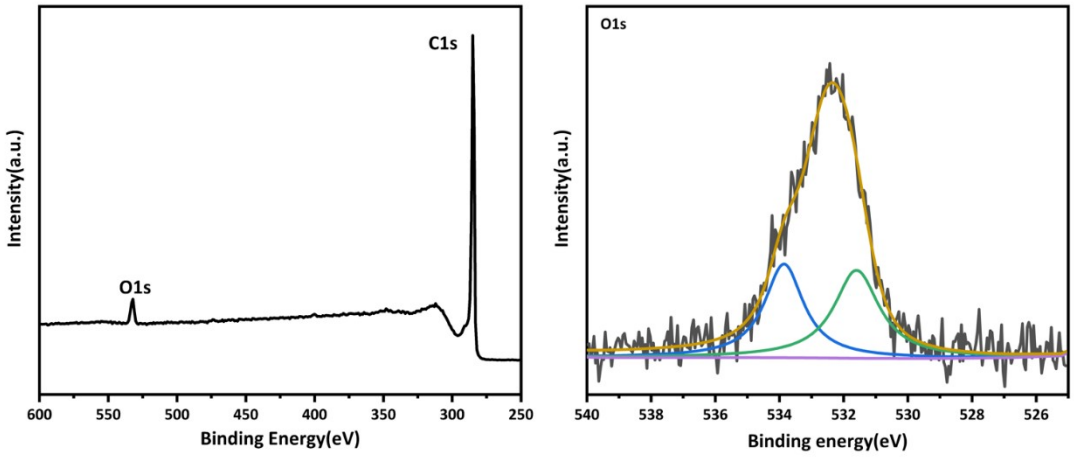

Figure S4.XPS spectrum of the graphene tubes.

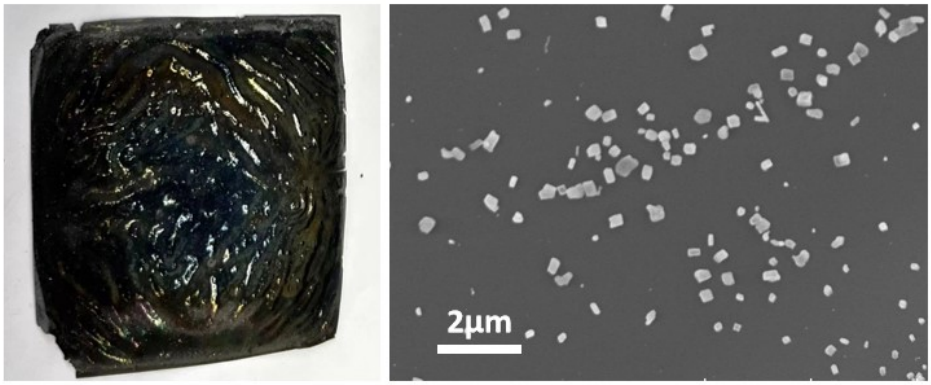

Figure S5. Result of the tube furnace treated PI/$CaCO_3$ film, CaO crystals can be seen on the surface but without graphene tube growth.

Table S1. The calculation results of TG-MS.

Gas	m/z	PI/$CaCO_3$ film	Pure PI film
H_2	2	23.48%	27.45%
CH_4	16	7.64%	7.75%
H_2O	18	6.07%	9.72%
CO,N_2	28	44.27%	29.83%
CO_2	44	18.54%	25.24%