Electronic Supplementary Material (ESI) for Nanoscale

Supplementary Information

Highly water-soluble multi-walled carbon nanotubes amine-functionalized by supercritical water oxidation

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Synthesis of multi-walled carbon nanotubes

High-purity MWNTs (99%) were produced by the catalytic reaction of ethylene over a Fe/MgO catalyst at 900 ˚C in an Ar/H_2 atmosphere. Briefly, a mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (99%, Aldrich) was dissolved in DI water and then a solution of Fe was added to the solution of MgO powder and DI water, followed by sonication for 1 h to embed the Fe metallic catalyst on the MgO powder. After baking and grounding the catalyst, ~50 mg of the catalyst was placed in a quartz boat that was inserted into the center of a quartz tube (i.d.: 30 mm, length: 800 mm) . A mixture of Ar:H_2/C_2H_4 was introduced into the quartz tube at a flow rate of 1300 sccm (Ar:H_2/C_2H_4 , 500:500/300) and a temperature of 900 °C for the production of the MWNTs. The flow rate of Ar:H_2/C_2H_4 was maintained for 100 min before the furnace was cooled to room temperature in an Ar:H_2 environment. The produced MWNTs had an average diameter of 20 nm and the number of graphite layers was about 15.

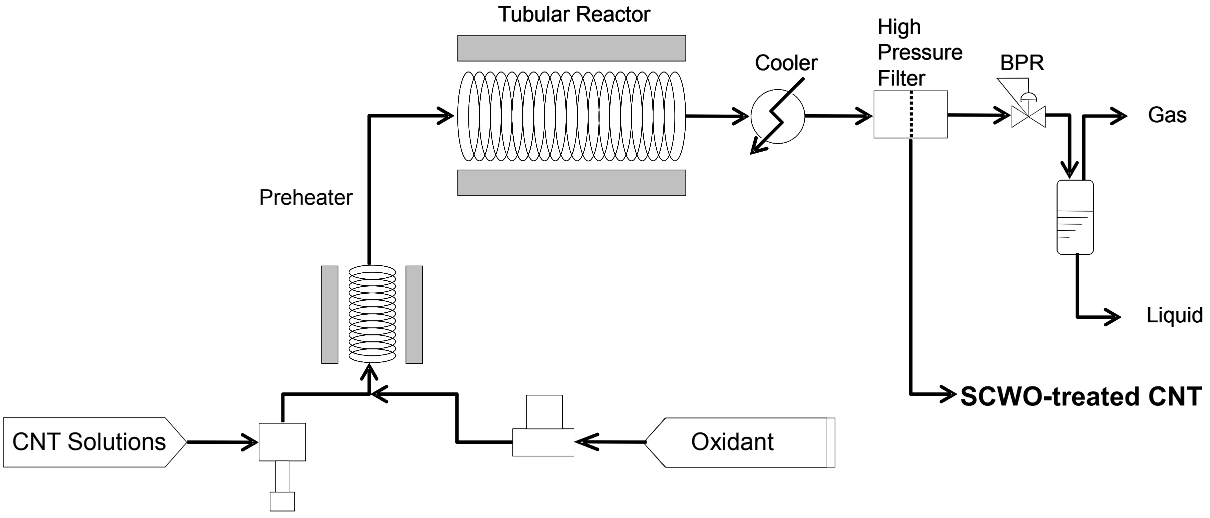

Figure S1. Schematic diagram of supercritical water oxidation (SCWO) system.

Operation procedure: (1) Preparation of 1 wt. % of MWNT mixture in water, (2) high pressure feeding of the above MWNT solution, (3) high pressure feeding of oxidant, (4) preheating, (5) surface treatment of MWNT in supercritical water condition, (6) cooling down the SCWO-treated MWNT solution, (7) separation of SCWO-treated MWNTs and water from the high pressure filter, (8) reduction of pressure.

The continuous SCWO apparatus for producing the amine-functionalized MWNTs includes a preheater, a reactor, a cooling down and depressurizing unit, and a product storage tank. The reactor of SCWO apparatus was a continuous type made of Inconel, 250 meter in length with an outer diameter of 9/16 in. The injection flow rate of MWNT aqueous dispersion was 100 kg/hr. 1 wt% of as grown MWNTs in aqueous system is a kind of slurry. In order to avoid aggregation, it stirred with agitator in injection tank during experiment. Oxygen gas was injected at 1.0 equivalent in proportional to carbon equivalent of MWNTs. 30 % of ammonia water was put into the MWNT aqueous dispersion at a molar ratio of 0.1 to 0.3.

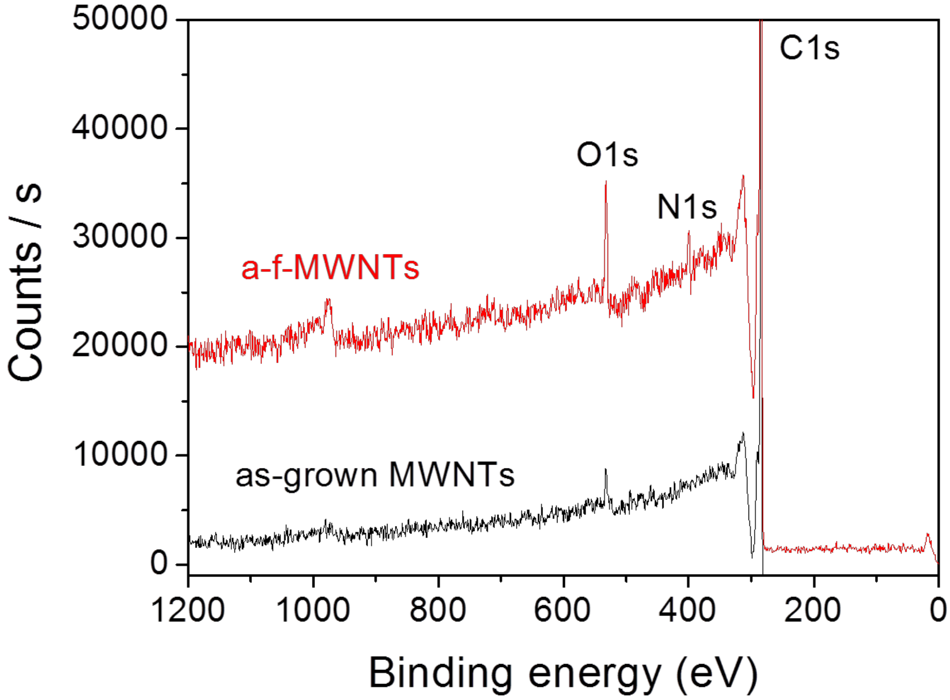

Figure S2. XPS spectra using 1486.6 eV of a-f- MWNTs and as-grown MWNTs.

As shown in Figure S2, the typical C1s, O1s and N1s spectra detected for a-f-MWNTs. C1s and O1s peaks of as-grown MWNTs corresponds to 284 and 532 eV, respectively. In comparison to as-grown MWNTs, a-f-MWNTs have higher intensity of O1s and new N1s (399 eV). This result indicates that the SCWO leads to the amination and oxidation.

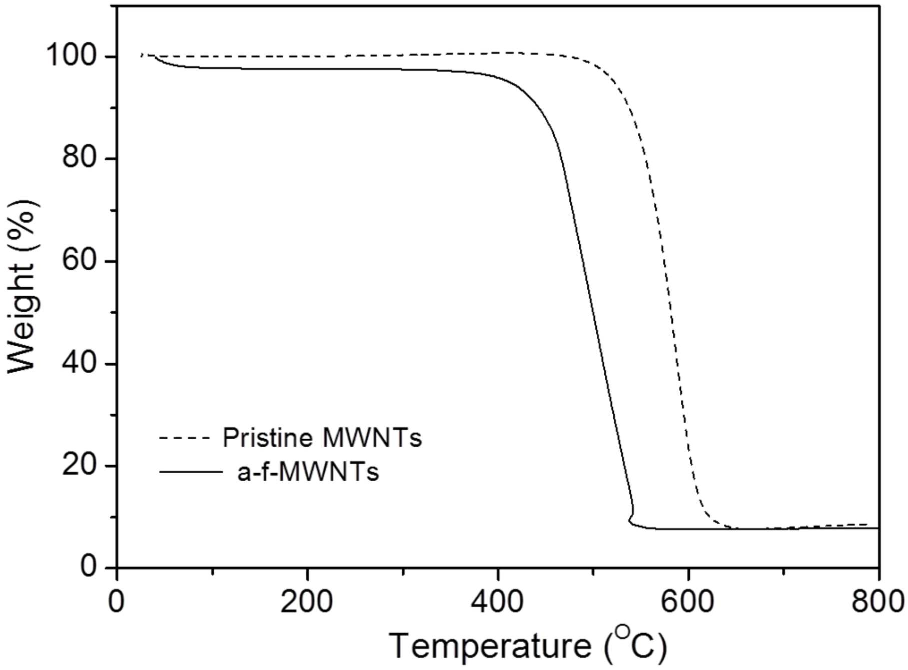

Figure S3. TGA curves of the as-grown and SCWO-treated MWNTs under an air atmosphere at a heating rate of 5 °C/min.

Figure S2 shows TGA curves for each MWNTs, respectively. The decomposition was carried out in air ambient at a low heating rate of 5 °C/min. As shown in this Figure, after SCWO treatment, the thermal decomposition temperature of MWNTs is decreased as a factor of 10 %. In addition, less than 430 °C, some weight loss of MWNTs is observed, indicating that defective or functionalized sites on the surface of CNTs may be generated. Also, after SCWO treatment, the gasification temperature is shift to the left, which means that the crystallinity of graphene at the surface of MWNTs is degraded due to SCWO treatment. This result is very consistent with Raman result in the Fig.3.