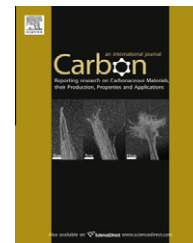


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One-pot synthesis of MnO₂/graphene/carbon nanotube hybrid by chemical method

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ABSTRACT

A branched hybrid of MnO₂/graphene/carbon nanotube (CNT) is generated in a one-pot reaction process by chemical method. Some ultrathin MnO₂/graphene nanosheets, around 5 nm in thickness, are randomly distributed on the CNT surface. Morphology, phase structure, microstructure and vibrational properties of the hybrid were characterized by field emission scanning electron microscope, X-ray diffractometer, high resolution transmission electron microscope and Raman spectrometer. Elemental distribution of the hybrid was determined by energy dispersive X-ray mapping performed in scanning transmission electron microscope mode. The key factor of the formation mechanism is associated with both redox and oxidation–intercalation reactions. Graphene flakes are partly exfoliated from the surface layers of the CNTs, and the redox reaction between KMnO₄ and hydroxyl groups occurs on both sides of these flakes, resulting in the formation of a MnO₂/graphene/CNT hybrid. Brunauer–Emmett–Teller surface area measurements indicate that the hybrid has over four times the specific surface area of the pristine CNTs.

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1. Introduction

Graphene and carbon nanotubes (CNTs) have driven numerous applications in electronics due to their outstanding physical and chemical properties [1–3]. Benefiting from their superior electrical conductivity, high electrochemical stability, good mechanical properties and high specific surface area, both graphene and CNTs are considered as ideal reinforcing components in fabricating complex nanostructured hybrids and composites, thereby tailoring properties of various nanostructured devices.

Manganese oxide (MnO₂) is a widely used material featuring low-cost, high energy density, environmental pollution-free and nature abundance [4,5]. Recently, much efforts have

been focused on the synthesis of nanoscale MnO₂/CNT (graphene or porous carbon) hybrids due to their significant electrochemical applications [6–10], such as supercapacitors and lithium ion batteries. However, there are still some challenge to be overcome such as increase of the mass loading on the surface of substrate, effective control of the thickness of MnO₂ films. Generally, MnO₂ deposits readily form planar nanosheets on flat substrates, resulting in the reduced surface area of substrates and thick MnO₂ layers coating [11]. For MnO₂/CNT composites, Reddy et al. [10] synthesized the coaxial hybrid of MnO₂ and CNTs leading to enhanced Li storage properties. In their further work, they [12] fabricated Au segmented MnO₂/CNT coaxial arrays which showed improvement in specific capacitance, energy and power density

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because of their good electrical contacts between electrode and current collector. Lee et al. [13] obtained MnO₂/CNT composite with well-controlled ultrathin MnO₂ films with an approximate thickness of 5 nm. This value is in agreement with nanoscale MnO₂ which could provide high specific capacitances. The design and fabrication of MnO₂/CNT composites with three-dimensional multifunctional architectures make the MnO₂ sheets grow along radial direction from the walls of CNTs, which is another possible way to dissolve mentioned problems [14]. Zhang et al. [15] found that MnO₂ tends to nucleate at the junctions of CNTs and then grow radically from junctions. These MnO₂ nanoflowers/CNTs arrays are composite with hierarchical porous structure. Xia et al. [16] pre-treated CNTs with KMnO₄ in neutral conditions to form small nanocrystals of MnO₂ on the CNT walls, and then the nanocrystals continuously grew into nanoflaky via a hydrothermal process. The key factor of formation of nanoflaky/CNTs composites is that the nanocrystalline MnO₂ on walls of CNTs serves as the nucleation site. Using graphene as the carbon support, Yan et al. prepared graphene/MnO₂ by microwave irradiation. The graphene sheets serve as high conductive support, which provide the large surface for the deposition of nanoscale MnO₂ particles. Wu et al. [17] mixed MnO₂ nanowires with graphene sheets by solution-phase assembly. Presence of MnO₂ nanowires on the surface of graphene prevents the stacking of graphene due to the van der Waals interactions, while on the other hand, the high conductivity of graphene is favorable to improve the dispersion of MnO₂ nanowires and the electrical conductivity. To the best of our knowledge, controlled synthesis and detailed structural scrutiny of MnO₂/graphene/CNT ternary hybrid have not been reported yet.

In this paper, we report a versatile chemical reaction process for fabricating a kind of three-dimensional hybrid of MnO₂/graphene/CNT nanostructures. At the low level of oxidation, oxygen-containing groups increased without MnO₂ nanocrystallines formed. The defects on the walls of CNTs is favorable to intercalation of SO₄²⁻ and peeling off of graphene. Afterwards, the partly exfoliated graphene came from the walls of CNT matrix, with the ultrathin MnO₂ sheets coating on the surface of graphene sheets instead of CNTs. Via strong van der Waals interaction of the un-exfoliated walls and MnO₂ film coating on the graphene and CNTs, the petal sheets of MnO₂/graphene could stand on the CNT matrix stably. Careful engineering of hybrid reached over four times the specific surface area of the pristine CNTs.

2. Experimental

2.1. Synthesis of multi-wall carbon nanotubes

The multi-wall carbon nanotubes (MWCNTs) in this work were synthesized by an aerosol-assisted chemical vapor deposition method (Supplementary data Fig. S1). At the beginning, a porcelain substrate was placed in a quartz tube, in which an argon flow (200 sccm) was passed through to purge the system for 20 min. Then the furnace was heated to 900 °C within 15 min. As soon as the temperature at the center of the furnace reached 900 °C, an aerosol (solution containing 11 g of

ferrocene (FeCp₂) in 500 ml of m-xylene) was generated ultrasonically and carried by mixed gas flow of argon A (40 sccm), hydrogen (60 sccm) and argon B (45 sccm, dilute gas) into the quartz tube, and meanwhile water vapor was introduced into the reactor by another flowing argon (40 sccm) through a water bubbler during the growth period. After 30 min of reaction, the ultrasonic sprayer was turned off and argon A was stopped. Hydrogen, water vapor and argon B flow were kept passing through the reactor until the furnace cooled down to room temperature.

2.2. Synthesis of MnO₂/graphene/CNT hybrids

In a typical procedure, MWCNTs (10 mg) were ground with KMnO₄ (100 mg, Aldrich) crystallites by using a mortar and pestle to a powder mixture. This mixture was then suspended in 10 ml de-ionized (DI) water and stirred at room temperature (22 °C) for different time of 1–12 h. After that, a trace amount of concentrated H₂SO₄ (50 μl, Aldrich, 95–98 wt.%) was introduced into the system and the stir continued at room temperature for additional 60 min. Afterwards, the solution was heated in an oil bath at 80 °C for 60 min. The reaction mixture was then removed from the heat source, and poured into 500 ml of DI water to cool down and dilute. The solution was filtered over a polytetrafluoroethylene membrane (0.22 μm pore size, Aldrich), and the remaining solid was washed repeatedly with DI water for several times.

2.3. Sample characterization

Morphology of the hybrid was characterized by field emission scanning electron microscope (FESEM, Hitachi S-4800). Phase structure of the hybrid was characterized by Bruker D8 micro X-ray diffraction (XRD), operating at 40 kV and 40 mA, with Cu K_α radiation (λ = 0.15418 nm). High resolution investigation of the hybrid was performed with transmission electron microscope/scanning transmission electron microscope (TEM/STEM, JEOL 2010F) equipped with an Oxford INCA Pentafet spectrometer (Oxford Instruments, Abingdon, Oxfordshire, UK). The acceleration voltage was 200 keV. Energy dispersive X-ray mapping (EDX) was performed in STEM mode with a probe size of 1 nm. Raman spectra were collected using Raman Rxn1-785 spectrometer (Kaiser Optical Systems, Inc.) Brunauer–Emmett–Teller (BET) surface area was measured by N₂ physisorption at 77 K using a Micromeritics ASAP 2010. Fourier transform-infrared (FT-IR) measurements were carried out by the KBr method using a Nicolet 6700 FT-IR spectrometer. FT-IR spectra were recorded in the transmittance mode over the range of 500–4000 cm⁻¹ by averaging 16 scans at a resolution of 4 cm⁻¹.

3. Results and discussion

Fig. 1A and C shows FESEM images of the hybrid, with the morphology of reticular and curved petal-like walls on the carbon nanotubes with originally smooth surface over the entire longitudinal length. Fig. 1B and D depict corresponding TEM images of inherent structure of the petals-tube hybrid, displaying a long-range array of transparent petal-like sheets

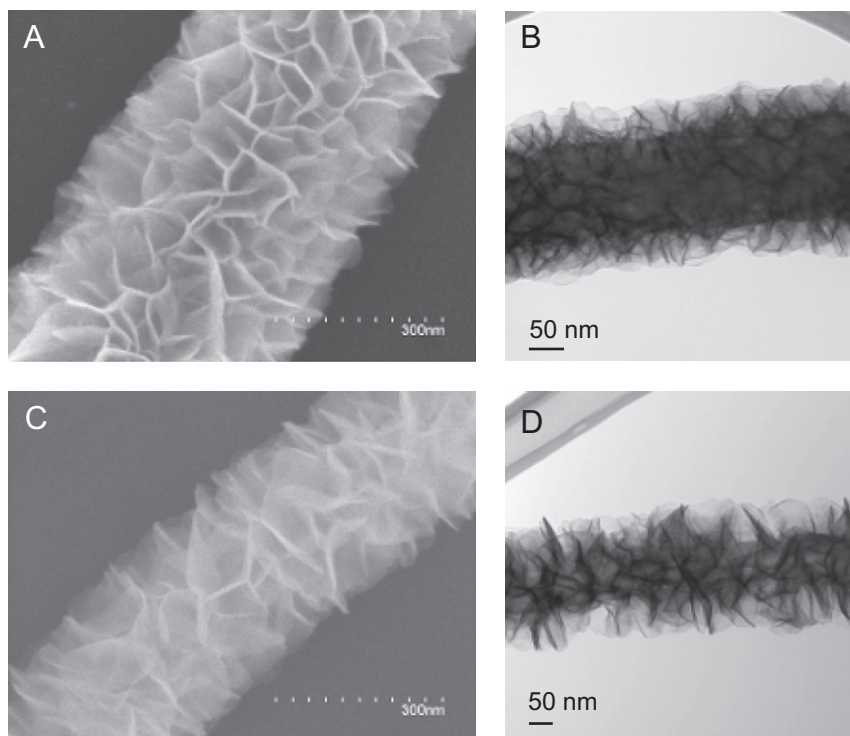


Fig. 1 – (A–D) SEM and TEM characterization of a representative MnO₂/graphene/CNT hybrid.

attached upon the sidewalls of the inner nanotubes with the size of ~280 nm. Interfacial profiles between the petals and the tube can be well distinguished. A BET surface area test shows that specific surface area of the hybrid is 143 m² g⁻¹,

presenting a over four times the specific surface area of the pristine carbon nanotubes (32 m² g⁻¹).

We used XRD analysis to determine the phase structure of the hybrid Fig. 2A. An evident peak at the 2θ value of about

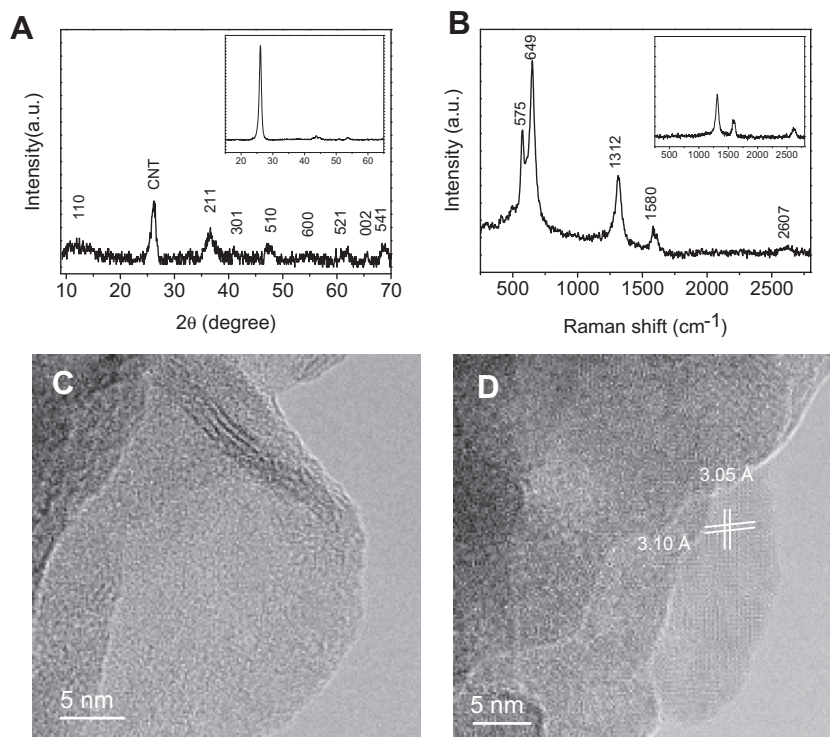


Fig. 2 – (A) XRD patterns of pristine CNTs (inset) and the hybrid. (B) Raman spectra of pristine CNTs (inset) and the hybrid. (C) High-resolution TEM (HRTEM) image obtained from a curved edge of the hybrid. (D) HRTEM image of a single petal-like sheet.

26.05° is consistent with (002) crystal plane of graphite. Other characteristic peaks with marked crystal faces can be assigned to the tetragonal phase of α -type MnO_2 (JCPDS 44-0141) [18,19]. We also used Raman spectroscopy to investigate vibrational properties of the hybrid Fig. 2(B). Intensity ratio of D to G band (I_d/I_g) increases accordingly from 1.53 to 2.77 with the oxidation reaction progress, indicating the enhanced level of disorder within the product and the formation of sp^3 carbon by functionalization. In addition, two sharp, low frequency bands at about 575 and 649 cm^{-1} can be used to characterize the tunnel species of α -type MnO_2 materials, which are commonly attributed to the Mn–O stretching vibration in the basal plane of MnO_6 sheet, and the symmetric stretching vibration Mn–O of MnO_6 groups [20,21]. Moreover, the edge of a representative petal-like sheet Fig. 2C was ascertained by high-resolution TEM, showing the thickness below 5 nm and counted with four layers or less considering the stacking possibility of two or more curving sheets. Two lattice fringes with the spacing 0.305 and 0.310 nm Fig. 2D can be indexed as (130) and (310) crystal planes of α -type MnO_2 , respectively, which is consistent with XRD and Raman observations.

The energy dispersive X-ray mapping performed in scanning transmission electron microscope mode is demonstrated in Fig. 3. Fig. 3A shows a TEM image of a representative segment of the hybrid, a bare carbon nanotube segment is indicated in the circle area of the picture. Fig. 3B–D shows elemental distribution of C, Mn and O in the hybrid. Besides strong signal of the CNT inner core, the mapping results indicate that the distribution of C, Mn and O elements is homogeneous throughout the petal-like nanosheets, implying that the nanosheets are composed of manganese oxide and C. The mapping results in the circle area reveal that the bare

nanotube is composed of only carbon without manganese oxide coatings.

Previous reports have indicated that two kinds of structures can be obtained in a CNT- KMnO_4 system under different conditions. If strong acid was introduced into the system, CNTs were cleaved in the longitudinal direction and unzipped to graphene ribbons under stronger oxidized environment without forming nanostructured MnO_2 [22]. If the level of oxidation is weaker, the MnO_2 nanocrystallines will nucleate on the defective sites of CNTs and then grow into the sheets coating on the CNT surface [16]. Based on the above characterization, it seems that our results are different from the two cases. Commonly, two kinds of reactions may take place in a CNT- KMnO_4 system. One reaction (A) is oxidation–intercalation–exfoliation [16,23]. Carbon nanotubes are considered as the graphite curved along one dimension with stacks of graphene. Depending on the π -conjugated network and van der Waals interactions of carbon atoms, the crystal structure of CNTs is stable. When the oxygen groups are introduced on the CNT walls, spacing of external layers is increased. The graphene sheets can be cleaved from the walls of carbon nanotube during an oxidation–intercalation process, which was demonstrated by Kosynkin et al. [22]. Although the strong π - π bonds exist in the walls of the MWCNTs, the surface oxidation could disrupt the π -conjugated network and liberate graphene sheets from the nanotube. The open degree depends on the level of oxidation. If the MWCNTs were treated under weaker acidic conditions, the walls would be partly exfoliated. The un-exfoliated parts of the walls could link the graphene to the MWCNTs.

Another reaction process is oxidation–reduction [24,25]. When the redox reaction is occurred between carbon and KMnO_4 in acid solution, it is as follows:

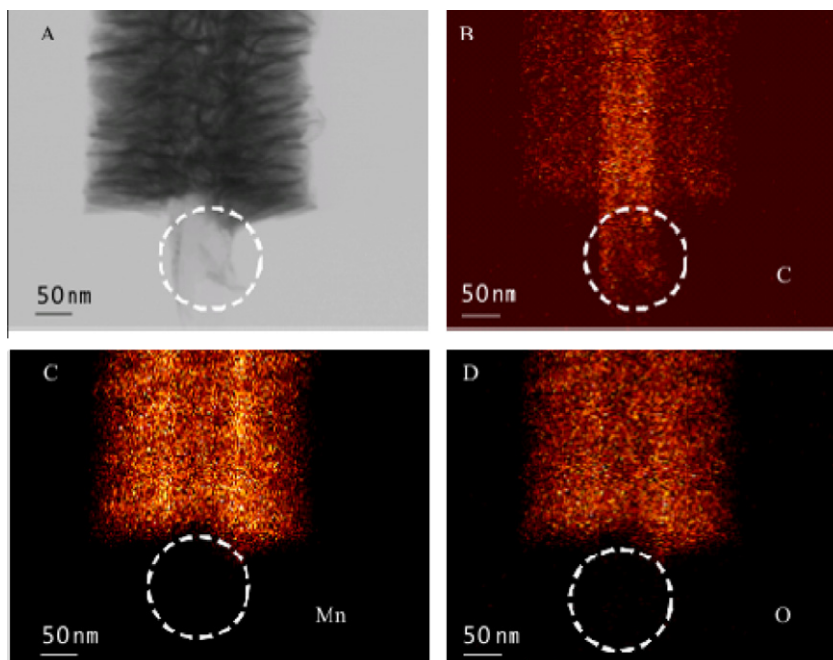


Fig. 3 – (A) TEM image of a representative hybrid segment with and without petal sheets surrounding the CNT. (B–D) STEM-EDX mapping results for C, Mn and O elements.



In this reaction, the graphene sheets serve as the sacrificial reductant and convert the Mn^{+7} to Mn^{+4} and thereby nanostructured MnO_2 are produced. As Yan et al. [11] reported, synthesis of MnO_2 nanocrystals was promoted through the rapid nucleation on the graphene surface under microwave irradiation with short reaction time, and the MnO_2 particles dispersed at the edges of graphene layers. In our experiments, the high ratio of KMnO_4 to CNTs promoted the oxidation of the CNT walls instead of nucleation of MnO_2 , which is different from the previous research about the mechanism of three-dimensional MnO_2/CNT nanocomposites by Xia et al. [16]. In order to explore the role of KMnO_4 and H_2SO_4 during the growth of hybrid, some control experiments were carried out.

Fig. 4 shows the TEM images and Fourier transform infrared (FT-IR) spectroscopy of CNTs treated only with KMnO_4 before heat (Fig. 4a), and images of the CNTs treated with KMnO_4 and different amount of H_2SO_4 (Fig. 4c–e). Comparing

to the pristine CNTs, as shown in Fig. 4a, the CNT walls kept smooth without any MnO_2 nanocrystals observed when the nanotubes were only treated by KMnO_4 . And we used FT-IR spectroscopy to track the functional groups on the surface of KMnO_4 -treated MWCNTs (Fig. 4b). The spectra of the transformed MWCNTs illustrate the presence of the $\text{C}=\text{O}$ ($\nu_{\text{C}=\text{O}}$ at 1640 cm^{-1}), $\text{C}-\text{OH}$ ($\nu_{\text{C}-\text{OH}}$ at 1380 cm^{-1}) and the COOH/OH ($\nu_{\text{COOH}/\text{OH}}$ at 3400 cm^{-1}) [22]. With incremental exposure of the MWCNTs to KMnO_4 , these characteristic peaks stepwisely increase and broaden except the peak at 1380 cm^{-1} , the $\text{C}-\text{O}-\text{C}$ ($\nu_{\text{C}-\text{O}-\text{C}}$ at 3400 cm^{-1}) stretch appears in sample a–c, indicating an increase number of carboxyl and hydroxyl functionalities. All these functional group changes reveal that oxidation degree of the final MWCNTs is remarkably dependent on the KMnO_4 pre-treatment time. There is no observation of nanoscale MnO_2 .

In order to obtain further information of initial growth of MnO_2 and the exfoliation from CNTs, detailed high resolution TEM studies were carried out.

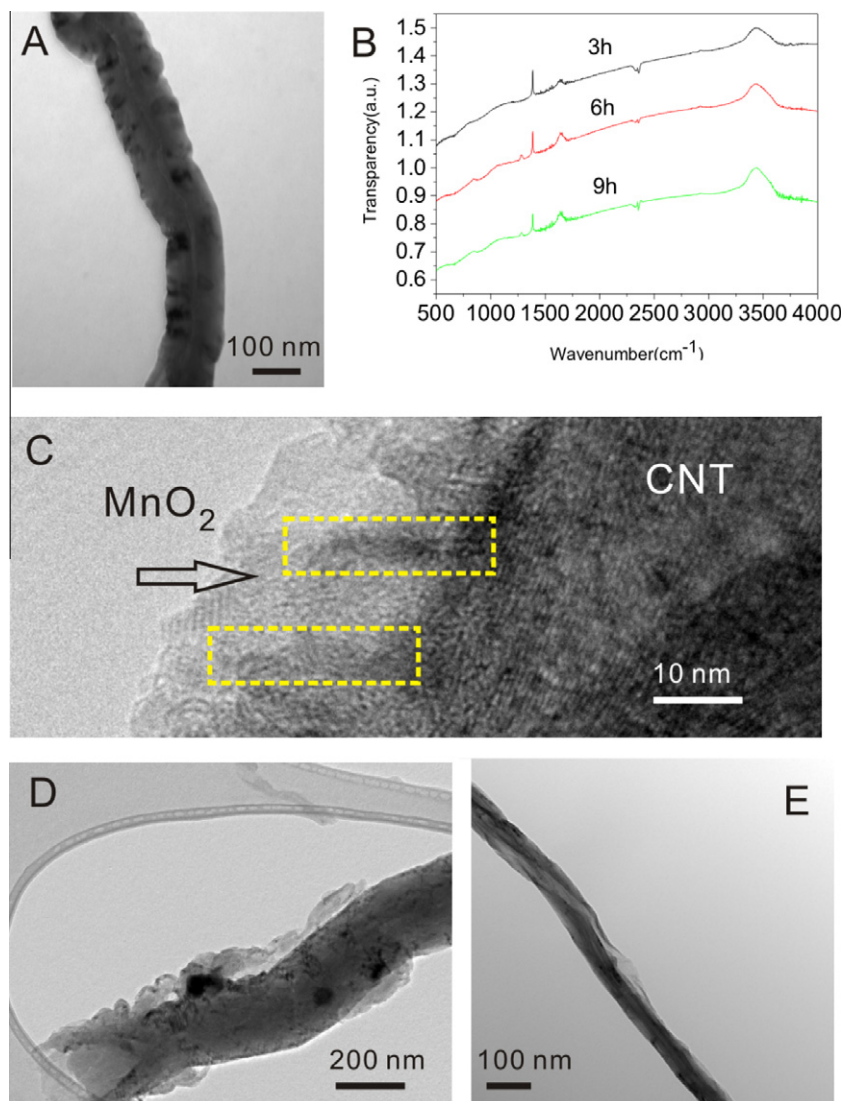


Fig. 4 – (A) TEM image of CNTs treated with KMnO_4 in water for 9 h; (B) FT-IR spectrum of CNTs treated with KMnO_4 in water for 3, 6, 9 h, respectively, TEM image of the CNT treated with KMnO_4 and, (C) 50 μl ; (D) 2 ml; (E) 10 ml H_2SO_4 .

Fig. 4c shows the TEM image of the initial growth of the hybrid based on the CNTs treated with KMnO_4 and low amount of H_2SO_4 (50 μl), same as the conditions of the sample shown in Fig. 1. The areas marked by the dotted border indicate that some petals were (about 10 nm long) partly exfoliated from the CNT, and the petals were surrounded by MnO_2 . When high amount of H_2SO_4 was used, the longitudinal unzipping of the nanotubes instead of MnO_2 deposition was observed as shown in Fig. 4d (2 ml of H_2SO_4), and Fig. 4e (10 ml of H_2SO_4).

Based on the above results, it indicates that the structure control of the hybrid in our work is expected to be dominated by a competition between the two reactions of oxidation–intercalation–exfoliation and oxidation–reduction processes, and the growth of MnO_2 /graphene/CNTs hybrid is proposed in this work by carefully controlling the growth parameters.

To get further insight into the structure of the hybrid, we ever adopted a general method to remove the excess of permanganate and MnO_2 , sufficient amount of hydrogen peroxide (H_2O_2) and a solution of HCl in water (1:10 v/v dilution from commercial concentrated HCl) were added and then the samples were washed by large amount of distilled water repeatedly. Fig. 5a shows TEM image of the samples after reduction, revealing that the spatial architecture of the sample is satisfyingly maintained. We used Raman technique to investigate the vibrational properties of the treated samples. Comparing to the samples without treatment, the Raman result shows the obvious change of characteristic peaks which belong to the MnO_2 . The peak located at 649 cm^{-1} disappears and the density of peak at 575 cm^{-1} is decreased, indicating

that the large amount of MnO_2 nanocrystals were destroyed after treatment. Furthermore, the density of the multi-band peaks around 2607 cm^{-1} (2D) are increased obviously, which is consistent with the multi-layer feature of graphene because of decrease of MnO_2 amount. This is also supported by the SEM–EDX results. The EDX reflects the mass loading of MnO_2 from 33% down to 5% (the range is 5–10%). It is still difficult to observe the details of their microstructure directly owing to the complexity of samples which are consisted of CNTs, MnO_2 and graphene-like carbon. Due to the coating of residual MnO_2 on the graphene-like petal sheet, and the 3-D architecture is stable even under stir or ultrasonic treatment. The presence of MnO_2 limited the characterization of the quality of the graphene sheet directly, even after the treatment of the samples with HCl and H_2O_2 to destroy the large amount of MnO_2 nanocrystals. Due to the non-uniform exfoliation of CNT walls and consumption of exfoliated graphene, the final state of graphene sheets can be: (1) completely exfoliated graphene sheets; (2) partly exfoliated graphene sheets attached on the CNT; (3) a sacrificial reductant and exhausted.

Besides dose of H_2SO_4 , the morphology of MnO_2 of the composites also strongly depended on reaction temperature and reaction time. Generally, higher temperature or longer reaction time would favor the gain of petal sheets formed. Keeping other optimized conditions the same, morphology and size of the carbon/ MnO_2 sheets were able to be readily modulated by adjusting each one of the three factors. Here dependence of the hybrid morphology on the temperature is taken as the example. Fig. S3 shows low and high magnification SEM images of the hybrids processed at 40, 60 and 80 $^\circ\text{C}$,

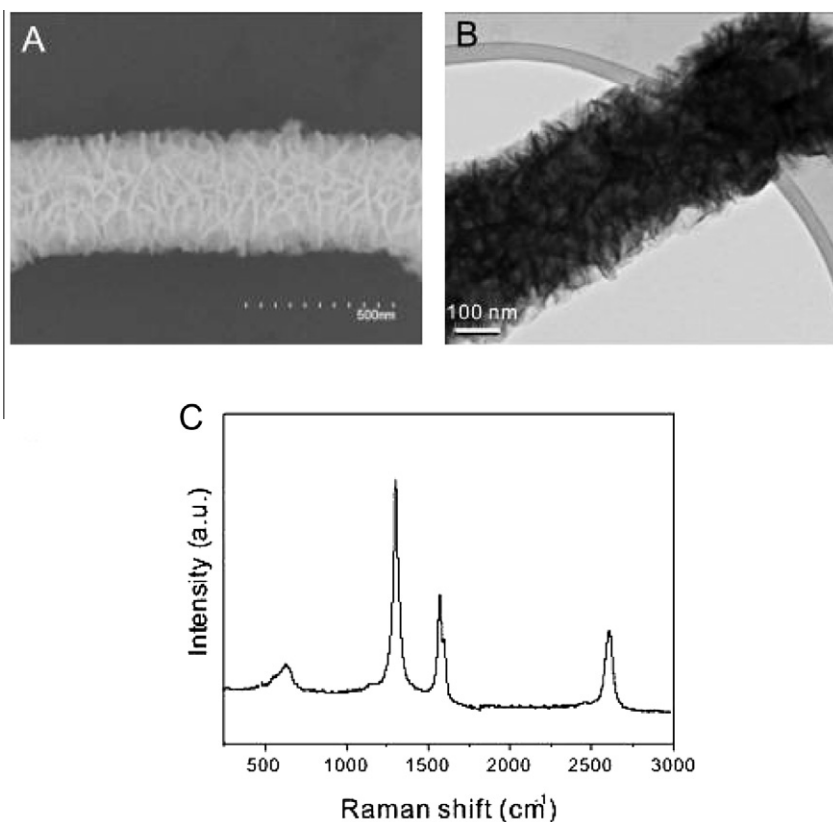


Fig. 5 – (A, B) SEM and TEM images of, (C) Raman spectrum of samples after HCl and H_2O_2 treated.

respectively, demonstrating stepwise growth of the petal sheets. At low temperature of 40 °C, the CNTs surface still remains relatively smooth except some corrugated structures. With the increase of the temperature, corrugated structure becomes entangled network and finally develops into the cross-linked petal-like structure on the CNT surface. The amount of H_2SO_4 had to be controlled as low as 1 ml, otherwise carbon/ MnO_2 sheets would be peeled off from CNTs (Fig. S4). Moreover, the CNTs would be unzipped in the longitudinal direction under large amount of H_2SO_4 . The treatment time of H_2SO_4 also needs to be carefully tuned to make the oxidation process more controllable. Long treatment time in the presence of H_2SO_4 could lead to the break of the hybrids into short segments (Fig. S5).

Depending on preparation processes, different carbon materials may exhibit different microstructures and properties, such as defects on surface, specific surface area and electrical conductivity. Therefore, we tried some usual carbon materials with the identical process, including graphene sheets, commercial MWCNTs with different diameters, flake graphite and spherical-like acetylene black which seem to be formed by graphene sheets in the scroll geometry. For the growth of the MnO_2 on the graphene sheets (Fig. S6), both flat and flower like structure can be found due to the difference among the local surface conditions of the graphene sheets. This indicates that MnO_2 is expected to be uniformly deposited on the graphene nanosheets depending on the

experimental conditions and quality of the graphene sheets. The morphologies of the received products grown on commercial MWCNTs and flake graphite substrates are similar to those grown from the MWCNTs in this work. We could observe the presence of a densely crossed array of the free-standing nanosheets with different size and curved shape in our samples with the commercial CNTs, and flake graphite inside (Figs. S7 and S8). However, in the case for acetylene black, the original carbon source exhausted and resultant hierarchical structure with hollow center was obtained. The low resolution SEM and TEM images (Fig. S9) of as-received samples show uniform changes of their morphologies and high yields. Besides few of the separate samples, most of which was still aggregated, being determined by the separate particles or aggregated chains of starting materials. TEM-EDX of single petal sheet shows the obtained sample is composed of four elements, namely C, K, Mn and O. This is different from the previous research on $KMnO_4$ -acetylene system [8], in which just MnO_2 nanostructures were obtained and the carbon source was released by generating CO_2 gas completely, revealing that large amount of carbon atom are composited with MnO_2 during the experimental process.

Thus, we suggest the following mechanism of the MnO_2 /graphene/CNT ternary hybrid demonstrating in the schematic as shown in Fig. 6: (1) on the initial stage, $KMnO_4$ is mixed with CNTs in a neutral condition. The large amount of $KMnO_4$ acts as a “weak oxidizing agent” due to much less

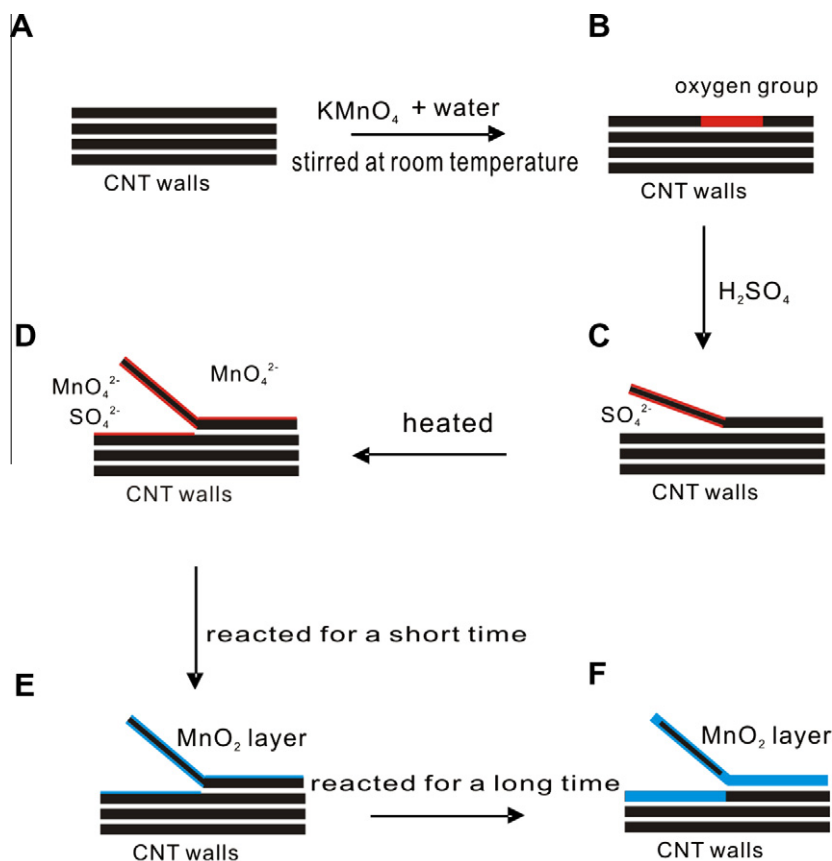


Fig. 6 – Schematic diagram of a proposed mechanism for the evolution steps from CNTs to MnO_2 /graphene/CNT hybrid.

positive electrode potential of the agent in a neutral condition than that in an acid ambient [26]. During the slow oxidation process, oxygen-containing groups would anchor spontaneously on the carbon nanotubes, especially on defective sites of the nanotube surface. However, the reduction of MnO_4^- by water is unfavorable. (2) When H_2SO_4 is introduced into the system, KMnO_4 in the acidic ambient leads to higher oxidation degree of the CNTs, which links those oxidized sites into curved epoxy chains (also called fault lines) and finally to various patterns [27]. Gradually, MnO_4^- ions are absorbed and precipitated on the oxidized location through the interactions between remained KMnO_4 and hydroxyl groups. The redox reaction is controlled kinetically at a very slow rate. (3) When the solution mixture is heated, oxidation degree of the nanotube sidewalls is significantly enhanced and SO_4^{2-} ions intercalate into the sidewalls preferentially along the “pattern” initiated by the epoxy chains. Since graphene flakes are partly exfoliated, reduction of large amount of Mn^{7+} to MnO^{4+} happens at both sides of the partly exfoliated graphene flakes, preventing the deposition of MnO_2 on the CNT surface.

4. Conclusions

The high yield and uniform hybrid of MnO_2 /graphene/CNT is synthesized by a multi-oxidation process. By adjusting the level of the oxidization, the π - π stacking of surface layers in pristine CNTs could be disrupted partly, which favors both intercalation and redox reactions happened on the graphene surface. The un-disrupted segment made sure the graphene remain on the CNT matrix stably, and final formed 3-D architecture with MnO_2 coating. This readily controlled process by coordinating the involved parameters makes it possible for the production of hybrid with well-defined structure in an industrial scale. The resultant structure can find great potential applications in developing various nanodevices in the field of electrochemical energy, catalysis and microelectronics. The present work may open a new door towards nano-electronics and other realms where hybridized structures are required.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2011.06.046.

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