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Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

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First published on: 08 April 2010

To cite this Article Fan, Qing-Qing , Qin, Zong-Yi , Liang, Xia , Li, Li , Wu, Wen-Hua and Zhu, Mei-Fang(2010) 'Reducing defects on multi-walled carbon nanotube surfaces induced by low-power ultrasonic-assisted hydrochloric acid treatment', *Journal of Experimental Nanoscience*, 5: 4, 337 – 347, First published on: 08 April 2010 (iFirst)

To link to this Article: DOI: 10.1080/17458080903536541

URL: <http://dx.doi.org/10.1080/17458080903536541>

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Reducing defects on multi-walled carbon nanotube surfaces induced by low-power ultrasonic-assisted hydrochloric acid treatment

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(Received 15 July 2009; final version received 7 December 2009)

A simple method to prepare multi-walled carbon nanotubes (MWCNTs) with high purity, high-aspect ratio and especially minimal defects is presented by low-power ultrasonic-assisted treatment of raw carbon nanotubes in hot concentrated hydrochloric acid under continuous reflux conditions. The evolution of surface morphology of MWCNTs during the treatment is evaluated by transmission electron microscopy, and microstructure is characterised by Fourier transform infrared and micro-Raman spectroscopy. The results show that with increasing the treatment time, the external layers with defects are peeled off piece by piece from the surface of MWCNTs until the inner graphite layers with good chemical resistance are exposed. The MWCNTs treated for less than 15 h by this method have been demonstrated to have minimal microstructural defects and large aspect ratios as compared to those treated in mixed concentrated nitric acid and sulphuric acid, which is further confirmed that almost no manganese dioxide particles can be anchored on the surface of the resulting MWCNTs due to their lack of the reactive defect sites.

Keywords: carbon nanotubes; defects; microstructure; acid treatment

1. Introduction

Many potential applications have already been identified for carbon nanotubes (CNTs), including conductive and high-strength composites, energy storage and energy conversion devices, sensors, field emission displays and nanosize semiconductor devices, due to their unique physical properties combined with high-aspect ratios and low density [1–3]. It has been demonstrated that nanotube properties are highly structured/size dependent and are influenced by the local atomic arrangement, nanotube diameter and length, morphology and nanosize structure [1]. Unfortunately, for raw CNTs, both single-walled and multi-walled (SWCNTs and MWCNTs, respectively) constitute of a rather complex

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mixture of structurally related materials with very widely varying properties. Therefore, the CNTs may find their limitations in some applications as they contain a large number of amorphous carbon particles and more defects along the graphene tube wall.

The MWCNTs comprise concentric graphitic cylinders with an interlayer spacing of 0.34 nm. Compared with SWCNTs, MWCNTs are lower cost, better availability and always conductive, which make them attractive materials for fabricating conductive polymer-based composites [4–6]. It is worth pointing out that the electronic properties of the perfect MWCNTs are rather similar to those of the perfect SWCNTs, because the coupling between the cylinders is weak in MWCNTs [1]. The electronic transport in MWCNTs occurs ballistically over long nanotube lengths, enabling them to carry high currents with essentially no heating. It has been reported that the MWCNTs have sustaining current densities greater than 10^9 A cm^{-2} [7], and their extraordinarily high current carrying capacity has been paid substantial attention to utilise CNTs in nanosize electronics [8]. However, if structural defects exist in the outer shell of the MWCNTs, its electronic and transport properties would be significantly lower as compared to the defect-free case. Thus, producing high-quality nanotube material in large quantities is essential to the potential applications.

The MWCNTs are generally regarded as passive filler materials for a new generation of high-performance composite, because of their exceptionally high Young modulus, bending strength and low density. Incorporation of nanotubes into polymer can potentially provide structural materials with dramatically increased modulus and strength [4–6]. Meanwhile, the low-loading levels and the nearly one-dimensional electronic structure of the MWCNTs allow improved conductivity to be achieved, while avoiding or minimising the deterioration of the original properties of polymer, such as mechanical properties and the low-melt flow viscosity needed for material processing. However, because of the pure carbon element and their stable structure, CNTs are insoluble in any organic solvents, which result in the applications of MWCNTs as reinforcing elements suffering from poor dispersion capability and weak interfacial interactions [2,4]. Therefore, modifying of the surface of MWCNTs is an essential prerequisite for improving the activity of MWCNTs and expanding their application areas.

Initially, purification of MWCNTs was performed using competitive oxidations in the gas phase [9], but due to limited yields, more attentions quickly were paid to aqueous oxidations, most frequently used strong acid and mixed concentrated acids [10–15], and sometimes alkaline hydroxides [16], hydrogen peroxide [17], potassium permanganate [18], chlorine water and ammonia water [19] and so forth. Unfortunately, although amorphous carbon and contaminating metallic catalyst particles can be successively removed, these procedures may lead to more defect introduction, local etching of nanotubes and even their structural damage. The sp^2 structure of the nanotube would be interrupted at the defect sites and, consequently, the electronic properties of the graphene would be altered. To meet the requirement of nanotube functionalisation, chemical reaction occurring on the surface must be controlled in a particular manner to ensure chemical modification of nanotubes as well as their initial properties [4,5].

The combination of the unique properties of MWCNTs with conjugated polymer makes these materials interesting multi-functional systems with great potential in many applications, such as supercapacitors, sensors, electromagnetic absorbers, photovoltaic cells and optical limiting devices and many more [20,21]. Therefore, the nondestructive

attachment of functional groups on the walls of nanotubes presents further challenge to experiment. Even if the outer wall loses its typical electronic behaviour, the nonfunctionalised inner walls can take over the charge transport. The weak attractive interactions between the MWCNTs and noncovalently attached groups are a potential drawback for stable energy conversion and strong interfacial interaction. Some interesting results on nondestructive purification and dispersion of the MWCNTs have been reported, such as rapid thermal annealing process using a DC vacuum arc discharge system [22], selective oxidation used alkaline hydroxides as activating agents [16], dispersing the MWCNTs in aqueous suspensions by the acid-exclusive method [23], purifying the MWCNTs in closed vessels by effecting microwave-assisted heating [24].

We report here a simple and efficient method to prepare MWCNTs with high purity, high-aspect ratio and especially minimal defects by low-power ultrasonic-assisted treatment of raw CNTs in hot concentrated hydrochloric acid (HCl) under continuous reflux condition. Herein, HCl as a relatively mild acid is not only applied to remove the amorphous carbon, but also peel off outer layers with defects from MWCNTs surfaces. Moreover, the residual acid can be completely removed during the drying procedure because of its high volatile. Ultrasonic irradiation is extremely used in common to break up aggregation of MWCNTs in solution processing [11,25], and herein strengthen the interaction between HCl and MWCNTs. Evolution of morphology and microstructure of MWCNTs during treatment is characterised and a model is presented to describe the change on the surface structure with the increase of treatment time. On the basis of the reaction, defects are necessary to achieve the selective deposition of metal oxide on surfaces of MWCNTs, *in situ* hydrothermal preparation of manganese dioxide (MnO_2) particles will be carried out using the resulting MWCNTs as a template for indicating them not suitable for nanosize particle decoration.

2. Experiment

Commercial MWCNTs (purity ≥ 95 wt%, about 55 ± 5 nm in diameter, about 12 ± 3 μm in length, chemical vapour deposition (CVD) method, Shenzhen Nanoharbor Co., China) were used as raw materials. All other reagents and solvents were supplied by Pinghu Reagent Company (Zhejiang, China) and were used as received or purified using standard procedures.

MWCNTs (0.1 g) were put into 150 mL concentrated HCl in 250 mL two necked, round-bottomed glass flask equipped with a reflux condenser. The flask was placed in an ultrasonic bath (Kunshan Ultrasonic Instrument, China, 90 W and 40 kHz) maintained at 70°C. During the treatment, samples of 10 mL were extracted at 3 h intervals up to 15 h. Then the samples were thoroughly washed using doubly distilled, deionised water, subsequently filtered on a 0.22 μm aperture cellulose membrane filter, finally dried at 110°C under vacuum for 24 h prior to analysis.

Hydrothermal synthesis of manganese dioxide (MnO_2) particles was carried out using the treated MWCNTs as a template in the solution of $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 . MWCNTs 0.1 g, 15 h-treated and 0.053 g oxalic acid were added into 10 mL deionised water in a flask. After ultrasonic irradiation for 0.5 h, 0.16 g KMnO_4 in 10 mL deionised water was added and the mixture was transferred to a Teflon-lined pressure vessel, followed by dropping 60 mL ethanol. After an 8 h reaction, the vessel was cooled down to

room temperature naturally. The resulting composite was filtered and washed with deionised water until neutral pH-value was reached, then the precipitate was dried at 100°C in the hot-air oven for 12 h. For comparison, synthesis of MnO₂ particles by using the untreated MWCNTs as a template were carried out under conditions similar to those mentioned above.

The morphologies of the treated MWCNTs and the resulting composites were characterised using an H-800 (Hitachi) transmission electron microscopy (TEM) and a JEM-2010 (JEOL) high-resolution transmission electron microscopy (HRTEM). A small number of the resulting MWCNTs were dispersed in ethanol, and then a drop of the dispersion was put on a holly-carbon copper grid for the TEM observation. The diameter and corresponding standard deviation of MWCNTs at various treatment times are evaluated from 20 positions in low-resolution TEM images. The infrared spectra were recorded on a Nicolet NEXUS 670 Fourier transform infrared (FT-IR) spectrometer, and the Raman spectra were recorded by a Renishaw spectrometer with a 50 mW Ar⁺ laser at 514.5 nm. The specific surface area was evaluated by nitrogen adsorption–desorption method.

3. Results and discussion

3.1. Morphology characterisation

Figure 1 shows typical TEM images of the treated MWCNTs at various treatment times. Rough surfaces of raw MWCNTs as shown in Figure 1(a) are resulted from the small number of amorphous carbon and metallic catalyst particles covered on outer surface of nanotubes. Initially, as shown in Figure 1(b), outer layers of MWCNTs become relatively smooth and the diameter of nanotubes decreases due to the removal of amorphous carbon and metallic catalyst particles attached on the surfaces of MWCNTs. At a later time, the treated MWCNTs can be seen to have an increase in surface roughness, and the accumulation effect of the removal of the outer layer for the MWCNTs can be clearly observed during the treatment. The rough surface of treated MWCNTs is attributed to the acidic etching of the CNT surfaces under ultrasonic irradiation. A significant uneven of nanotubes walls is observed for 9 h-treated MWCNTs as shown in Figure 1(c), wherein the diameter square deviation reaches the highest value up to 12 nm. This result can be attributed to an enlarge behaviour for the formation of the defective sites on nanotube surfaces, and the outer layer walls of MWCNTs are peeled off piece by piece; these fragments further break into more small pieces and finally float on the surface of water. Note that the treated MWCNTs have obvious changes in diameters, but less change in lengths. The reason that we do not see such damages in lengths might be due to the fact that the ultrasonic bath we used had a low-output power and low-treatment temperature under continuous reflux condition. After treatment for 15 h, as shown in Figure 1(d), smooth sidewalls of MWCNTs with the diameter of $38 \text{ nm} \pm 3 \text{ nm}$ are observed again, and no more damages can be found with the prolong of time, which implies that MWCNTs with smooth surface exhibit excellent resistance against HCl attack. After the treatment, about 48 outer layers of nanotubes are peeled off, and a significant loss of weight of raw MWCNTs about 30–40% can be observed. The HRTEM images of 15 h-treated MWCNTs (Figure 1(e) and (f)) indicate that the formation of closed-capped MWCNTs with minimal defects, whereas the nanotubes treated in the most

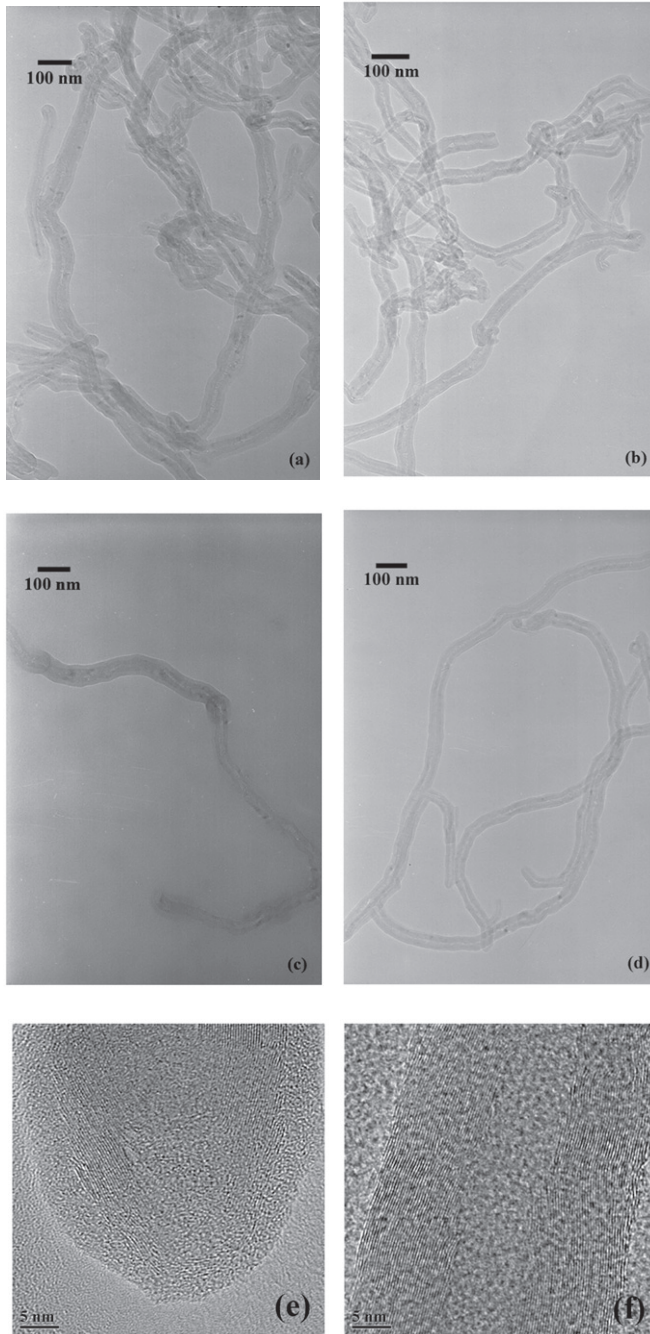


Figure 1. TEM images of MWCNTs treated at various times: (a) 0 h, (b) 3 h, (c) 9 h, (d) 15 h; and HRTEM images of MWCNTs treated for 15 h: (e) end and (f) sidewall.

commonly used mixture of concentrated nitric acid and sulphuric acid are generally seen with open ends, granular surface and short in length. Although significant changes occurred on the morphology of the MWCNTs, no obvious change can be observed on Brunquer-Emmett-Teller (BET) surface area with the increase of treatment time.

3.2. FT-IR spectra

The typical FT-IR spectra for the untreated and resulting MWCNTs for various reactive times are shown in Figure 2. Note that the intensities cannot be readily compared between spectra, due to the existence of the complex structures. In all the MWCNTs spectra, there is the strong absorption band around 3445 cm^{-1} ascribed to O–H stretching related to surface hydroxyl groups and water, and the weak peaks at 2920 and 2850 cm^{-1} are associated with the asymmetrical and symmetrical stretch of methylene (CH_2) which may relate to a low concentration of H-terminations on the surface of MWCNTs, or explicit amorphous carbon [10]. The band around 1580 cm^{-1} is associated with the stretching vibrations of C=C double bonds in nanotube backbone [18]. After the removal of amorphous carbon covered on the surfaces of MWCNTs, the band becomes more evident. The band around 1630 cm^{-1} is attributed to the H-bonded carbonyl groups ($\text{C}=\text{O}$) conjugated to the graphene wall, which originates from residual humidity in the pellet. For 3 h-treated and 15 h-treated MWCNTs, two new bands appear at around 1430 and 877 cm^{-1} might arise from adsorbing water in the graphene sheets of MWCNTs. No obvious band appears around 1718 cm^{-1} for all treated MWCNTs, which excludes the presence of oxygen-containing groups, contrary to the result obtained in mixed concentrated nitric acid and sulphuric acid.

3.3. Raman spectra

Micro-Raman spectroscopy is a powerful tool for structural characterisation of CNTs and related materials. As shown in Figure 3(a), all the spectra are normalised to the

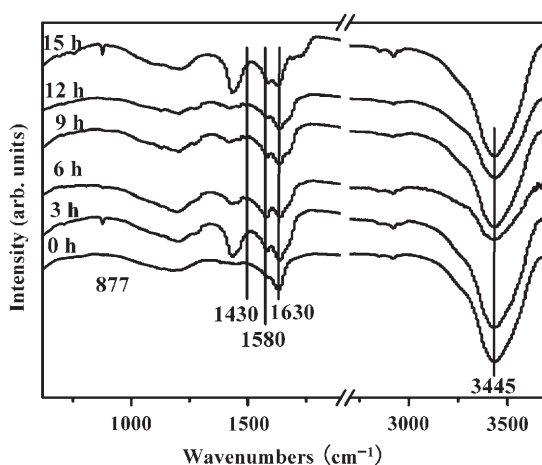


Figure 2. FT-IR spectra of the resulting MWCNTs treated at various reactive times.

intensity of the D band appear around 1347 cm^{-1} , and the splitting of the G band and the G' band is fitted with the mixed Gaussian–Lorentzian components. The well-defined G band appeared around 1576 cm^{-1} is related to the graphite E_{2g} symmetry of the interlayer mode, which indicates the structural integrity of the sp^2 -hybridised carbon atoms of the sidewall of nanotubes. In contrast, the broad peak near 1347 cm^{-1} is D band, which reflects the disordered sp^3 -hybridised carbon atoms and interprets the defects of nanotubes [13]. The D_0 band appeared as a weak shoulder of the G band at higher frequencies is a double resonance feature induced by disorder and defects.

The relative area of the D, D_0 and G bands is introduced to characterise the structural defective degree of the MWCNTs, and the decrease in the $(I_D + I_{D_0})/I_G$ ratio indicates the destruction of the graphitic integrity. The $(I_D + I_{D_0})/I_G$ as a function of the treatment time is shown in Figure 3(b), and the ratio decreases significantly after 3 h, which implies the removal of amorphous carbon on the tubes. Subsequently, the $(I_D + I_{D_0})/I_G$ gradually increases and reaches the maximum after 12 h, which corresponds to the increasing of the degree of disorder. This result can be attributed to the accumulative effect for the formation of the defective sites on the surfaces of MWCNTs. Then a dramatic decrease in the $(I_D + I_{D_0})/I_G$ ratio for 15 h-treated MWCNTs can be observed, which indicates that less defective outer layers of treated MWCNTs are exposed. This change is in accordance with the evolution of surface morphology for MWCNTs during the treatment is observed by TEM.

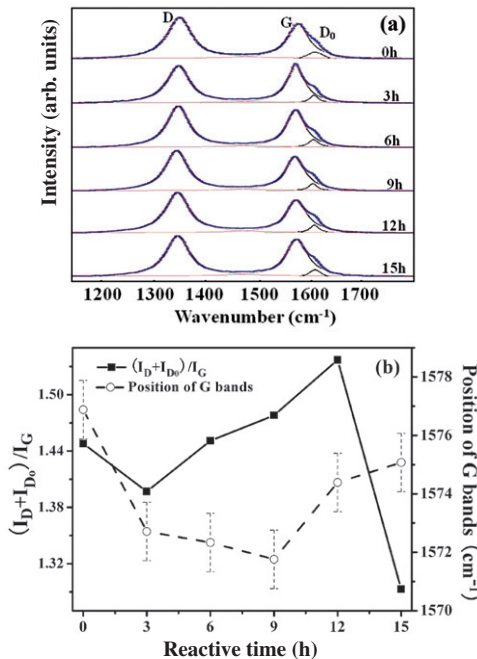


Figure 3. (a) Raman spectra of the untreated and MWCNTs treated for 15 h. The intensities are normalised to the D band about 1347 cm^{-1} for all spectra; and (b) the intensity ratio of D, D_0 , and G bands $((I_D + I_{D_0})/I_G)$ and the position of G bands for the resulting MWCNTs as a function of the treatment time. The decrease in the $(I_D + I_{D_0})/I_G$ ratio indicates the destruction of the graphitic integrity.

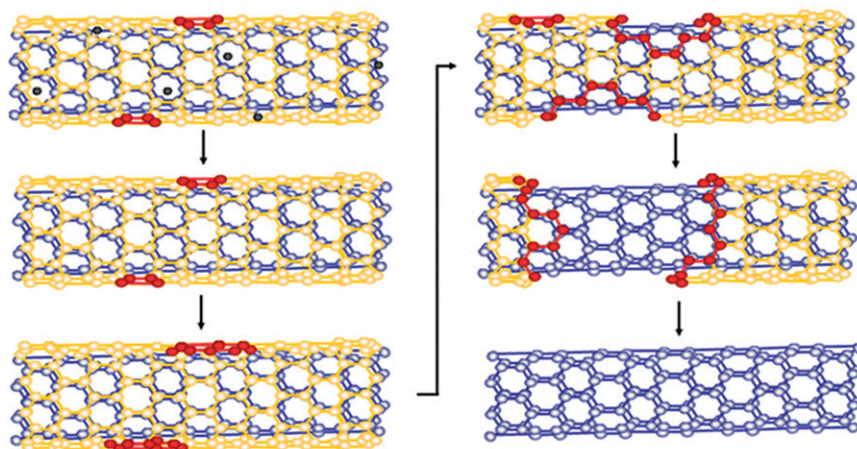


Figure 4. Schematic model of structural evolution during HCl-treated MWCNTs process.

It is demonstrated that the position of G band can give some important information of the microstructure of nanotube walls [26,27]. Downshift of G band implies the more polygonal and less cylindrical structural defects on the surfaces of MWCNTs [26], and the increasing number of nanotube layers [27]. We find that the downshift of G-peak from 1577 cm^{-1} for the untreated MWCNTs to 1572 cm^{-1} for 9 h-treated MWCNTs is observed, which indicates that more polygonal and less cylindrical structures remain in the MWCNTs. Then the frequency of G band gradually upshifts to 1575 cm^{-1} for 15 h-treated MWCNTs, which indicates less thin nanotubes with relatively more cylindrical structures are obtained. It is consistent with our TEM observation that the average diameter of HCl-MWCNTs decreases gradually from 46 nm for 9 h-treated MWCNTs to 38 nm for 15 h-treated MWCNTs.

3.4. Mechanism

Possible mechanism for reducing defects on the surfaces of MWCNTs induced by low-power ultrasonic-assisted HCl treatment is presented as shown in Figure 4. The black points in Figure 4 represent the impurities, such as amorphous carbon and residual metallic catalyst particles. When the raw MWCNTs are treated in HCl, the impurities can be removed gradually, meanwhile the reactive defect sites are attacked; the defective area gradually expands, accordingly, the outer layers with a large number of defects peel off piece by piece from the surface of MWCNTs. These fragments further break into more small pieces floating on the surface. This procedure is repeated until the inner graphite layers with good chemical resistance are exposed.

3.5. Selective deposition of nanoparticles on MWCNTs before and after treatment

It is reported that selective deposition of nanosize metal particles onto wall of CNTs due to the more reactivity of the defect sites than other nanotube lattices can be utilised for

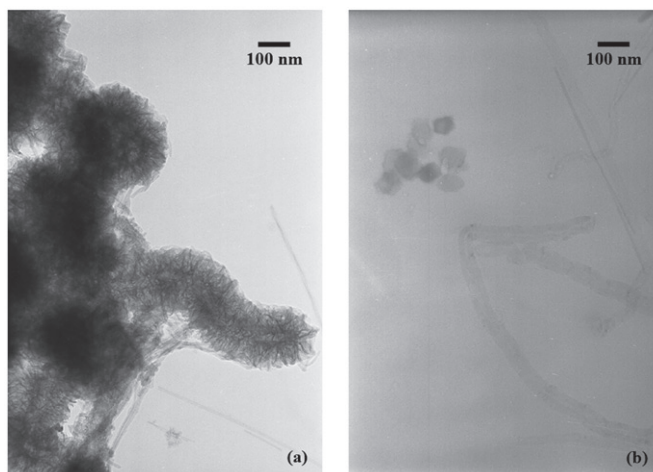


Figure 5. TEM images of MnO_2 particles prepared by hydrothermal reaction in the presence of (a) untreated and (b) treated MWCNTs.

finding fault with CNTs [28]. On the basis of the reaction, defects are necessary to achieve the selective deposition of metal oxide on surfaces of CNTs, *in situ* hydrothermal preparation of MnO_2 particles is carried out using the resulting MWCNTs as a template for further verification of minimal defects that appear on the resulting MWCNTs. Figure 5 presents the TEM images of MnO_2 particles prepared by hydrothermal reaction by using untreated and treated MWCNTs as a template, respectively. As shown in Figure 5, some needle-like MnO_2 particles anchor on the surface of the untreated MWCNTs, whereas some isolated MnO_2 particles appear around the nanotubes. This result demonstrates that original defects for raw MWCNTs are effectively reduced by low-power ultrasonic-assisted treatment in hot concentrated HCl under continuous reflux conditions.

4. Conclusions

A facile approach, low-power ultrasonic-assisted treatment of raw MWCNTs in hot concentrated HCl under continuous reflux conditions, is presented for preparing the MWCNTs with high purity, high-aspect ratio and especially minimal defects. An enlarged behaviour for the formation of the defective sites on nanotube surfaces is observed during the treatment. With the increase in treatment time, the defective outer layers of the MWCNTs are peeled off piece by piece until the inner graphite layers with good chemical resistance are exposed. Although the MWCNTs show obvious decrease in diameters, its original high-aspect ratio is kept. The reason for less damage in lengths can be contributed to the fact that the ultrasonic bath we used has a low-output power and low-treatment temperature under continuous reflux condition. The comparison between untreated and treated MWCNTs as a template for selective deposition of MnO_2 by hydrothermal reaction further confirm that the defects on the surface of raw MWCNTs can be effectively diminished by our presented method.

Acknowledgements

We greatly acknowledge the financial support from the Shanghai Pujiang Program (07PJ14005) and the Doctorate Innovation Foundation of Danghuo University (BC200905).

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