

## CHARACTERISTIC OF MILD ACID FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES TOWARDS HIGH DISPERSION WITH LOW STRUCTURAL DEFECTS

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Multiwalled carbon nanotubes (MWCNTs) have a great potential in wide applications but faces limitation in term of dispersion feasibility. The aggregation of MWCNTs floss has restricted its usage and thus, acid treatment is expected to promote the MWCNTs re-aggregation. The functionalization process of MWCNTs involves oxidation reaction using mild aqueous acid mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (1:3 v/v), via ultrasonication technique. The results were then confirmed by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Thermogravimetry Analysis (TGA), Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) analysis. From the FTIR spectrum, the existence of carboxyl group indicates the oxidation of MWCNTs on the outer surface wall. TEM and FE-SEM micrographs show the occurrence of surface modification on the MWCNTs structure. The method used in functionalization MWCNTs has created fragmented structure toward the functionalized MWCNTs. TGA analysis on functionalized MWCNTs also shows the presence of the oxygenated group decomposition. Finally, a well dispersed of MWCNTs colloidal was successfully obtained with less MWCNTs structure collapsed.

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### 1. Introduction

Carbon nanotubes is one of the carbon allotropes, comes with unique and distinctive in both mechanical and electrical properties. And since the discovery of carbon nanotubes firstly back in 1960 by M. Endo and then in 1991 by the Japan scientist named Sumio Ijima [1, 2], this nanomaterial has attracted huge attention among other scientists and researchers. Besides, the applications of carbon nanotubes in materials chemistry have been further developed, progressively. Carbon nanotubes were found to have great potential applications in various fields such as biosensors and nanobiotechnology and many others applications, due to the electrical conductivity and stability toward chemical reaction [3, 4, 5].

However, the critical difficulty in applying carbon nanotubes for applications is because of the poor dispersibility and bundling between carbon nanotubes tubules, as affected by the attractive van der Waals interaction among themselves [6]. Therefore, surface modification of carbon nanotubes through functionalization process is the way to overcome these problems. Carbon nanotubes functionalization is a process where the addition of functional groups onto the surface of carbon nanotubes is being generated. With the functional groups present on the CNTs

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surface, the dispersion of CNTs in aqueous media will be improved, depending on the selected functionalization media [6, 7].

Many works had study the MWCNTs functionalization, however the result on the MWCNTs structure were still required few modification. It is because, severe structure destruction of MWCNTs was occurred during the functionalization including the decapping that occurred at the end of the tubes and the cutting and breaking of the MWCNTs length [8, 9]. The structure destruction caused the changes of the MWCNTs valuable properties which are the main objective that we want to avoid. In this research, we are study the dispersion, chemical properties as well as the morphology of functionalized MWCNTs by acid treatment functionalization method in the low acid concentration. We are attempting to functionalize the MWCNTs with less structure disruption yet obtaining stable MWCNTs colloidal suspension.

## **2. Experimental**

### **2.1 Materials**

Commercialized MWCNTs were purchased from Sunnano with the purity of 90% according to the company specification, were used in this study. Sulfuric acid 95-97% ( $\text{H}_2\text{SO}_4$ ) analytical reagent grade was purchased from QRec while, nitric acid 65% analytical reagent grade ( $\text{HNO}_3$ ) was purchased from HmbG, were used as the functionalization media. All chemicals were used as-received without further purification.

### **2.2 Experimental**

In this study, MWCNTs were functionalized by using mixture of acid oxidation method [10]. Firstly, 100 mg of as-synthesized MWCNTs were treated with 20 mL of aqueous acid solution of  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture. To ensure that there is no massive structure destruction on MWCNTs, the 6M of nitric acid and sulfuric acid concentration were used in this study and the ( $\text{HNO}_3/\text{H}_2\text{SO}_4$ ) acid mixture was in the ratio of 1:3 by volumes per volume. Mixture of MWCNTs and acid solution were ultrasonically vibrated in water bath ultrasonic Branson 2000 at temperature of 40 °C for 4 hours. After that, the functionalized MWCNTs was collected via discard method and then washed thoroughly with distilled water until the neutral pH value of MWCNTs solution is approximately to pH 7, was obtained. Sample collected was then dried at ambient temperature using acetone. Finally, the dispersion analysis of functionalized and non-functionalized MWCNTs in acetone as the polar solvent was tested. In complementing the dispersion data, the detailed structures and the chemical compositions of as-synthesized MWCNTs and functionalized MWCNTs were characterized by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetry Analysis (TGA), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM).

## **3. Results & discussion**

### **3.1 Characterization**

Figure 1.0 shows the FTIR spectra of as-synthesized and acids functionalized MWCNTs. The individual IR spectrum of each samples were slightly changed with the purpose of improving the additional peaks appeared, accordingly with the effect on the chemical bonding of MWCNTs. After the acid treatment, there are few peaks signal were observed in the IR spectrum of the functionalized MWCNTs. The acid functionalized MWCNTs spectrum shows one weak peak appeared at around  $1700\text{cm}^{-1}$  which is ascribed to the present of C=O stretching mode of carboxylic groups and this particular peak can be observed clearly after the acid treatment.

For this study, the as-synthesized MWCNTs used were previously purified and a part of catalytic metallic nanoparticles from the catalyst residue were almost certainly eliminated during

the purification process. Thus, the less presence of residual catalyst in the MWCNTs IR spectra before and after purification process as was similar finding as reported by Singh *et al* (2006) showing that the high purity of MWCNTs [11]. On the other hand, the peak signal appeared at  $1540\text{ cm}^{-1}$  in both IR spectra of as-synthesized and acid functionalized MWCNTs is associated to the carbon nanotubes backbone stretching mode. The presence of this peak gave an idea that the structure of MWCNTs was preserved after undergone acid treatment. Besides, a weak peak was appeared at  $1400\text{ cm}^{-1}$  for acid functionalized MWCNTs which is associated to the O-H bending deformation mode of the carboxylic acid group.

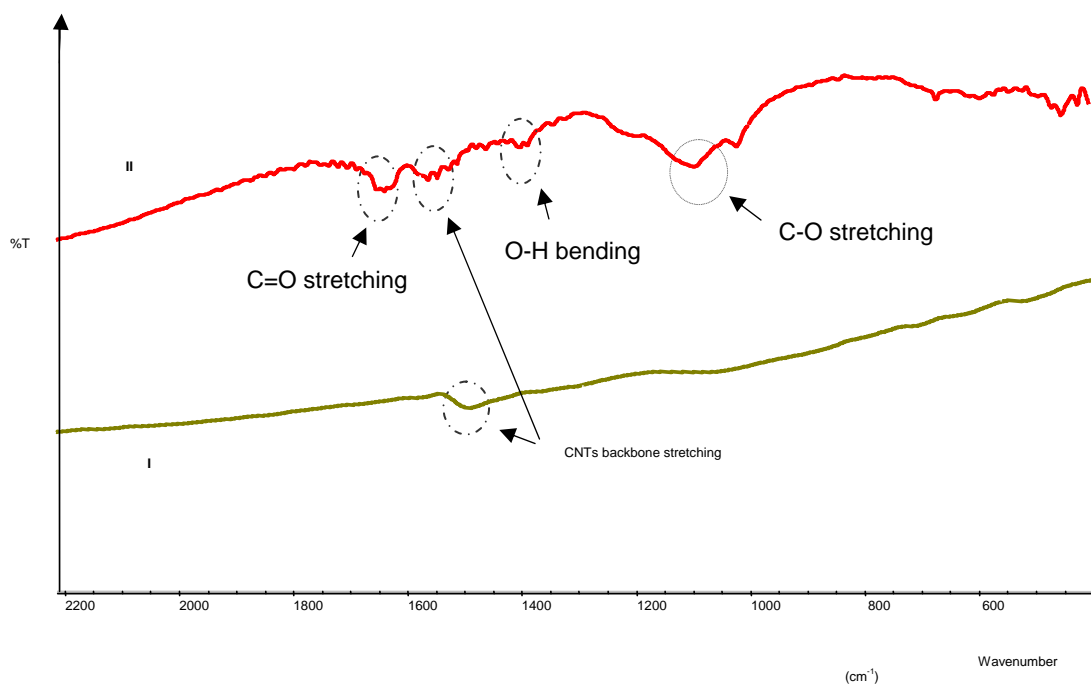


Fig. 1.0: FTIR spectrum for as-synthesized (I) and functionalized MWCNTs (II)

Figure 2.0 shows the x-ray diffraction patterns of as-synthesized and acid functionalized MWCNTs. As described in the previous works [12, 13], the significant diffraction pattern of the as-synthesized MWCNTs is appeared at  $2\theta$  of  $25.3^\circ$ . The  $2\theta$  peaks is corresponded to (002) reflection planes or also known as interlayered spacing between adjacent graphite layers, respectively. The (002) reflection peaks was observed at the same  $2\theta$  values in both as-synthesized and functionalized MWCNTs diffractions.

Interestingly, the intensity of diffraction peak at (002) in acid functionalized MWCNTs was increased as compared to the as-synthesized MWCNTs. This is an indication of the loosely of the carbon nanotubes floss after the acid treatment and form more ordered CNTs floss in the acid functionalized MWCNTs. Futhermore, from XRD patterns of the functionalized MWCNTs samples, it is shows that the XRD patterns are similar to the as-synthesized MWCNTs. From XRD patterns, it can be conclude that functionalized MWCNTs is still had same cylinder wall structure and inter planar spacing after the functionalization process. Thus, the structure of MWCNTs is protected even after undergone the acid treatment as confirmed from XRD analysis previously.

On the other hand, the thermo gravimetric analysis was used to determine the differences MWCNTs mass content after undergone acid treatment. The characterization of weight loss during oxidation of the MWCNTs sample, were run under air with heating from  $40\text{ }^\circ\text{C}$  to  $900\text{ }^\circ\text{C}$  at rate of  $20\text{ }^\circ\text{C}/\text{min}$ . From the TG thermogram, a significant weight loss started to occur at  $550\text{ }^\circ\text{C}$ . The weight loss continued to increase rapidly with the increasing of the temperature until the oxidation completed at  $900\text{ }^\circ\text{C}$ . This result implies that only small amount of impurities were present in the as-synthesized MWCNTs sample, as complemented in the FTIR data earlier. The as-synthesized

MWCNTs can be sure is highly in purity with lower contains of carbonaceous matter and catalyst residues.

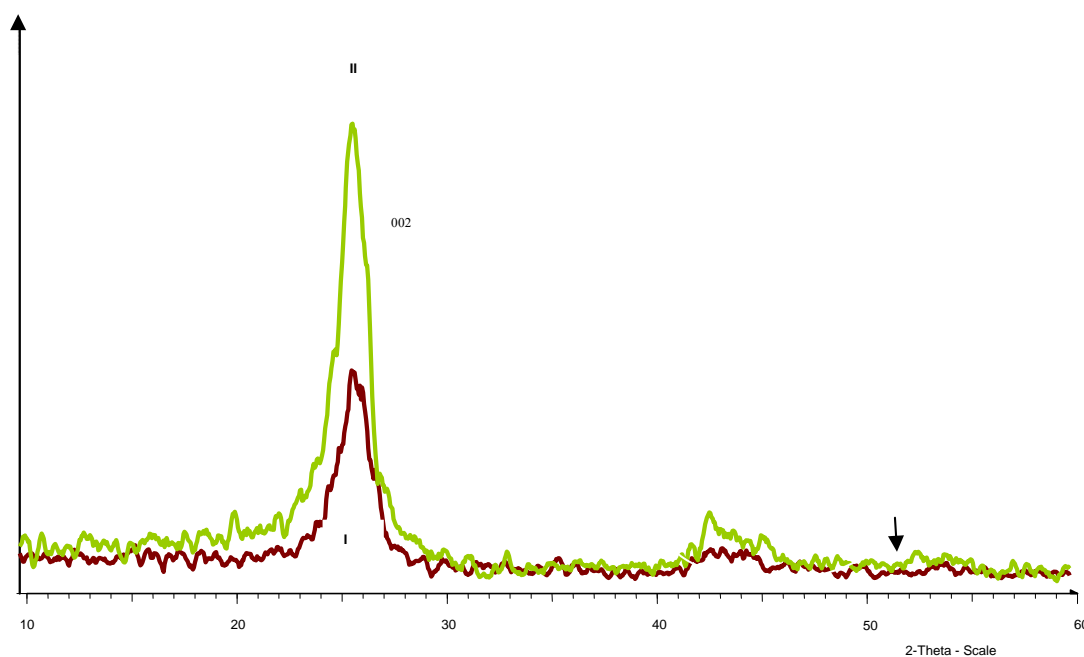


Fig. 2.0: XRD patterns for as-synthesized (I) and functionalized MWCNTs (II)

The TGA scan conditions were similar to those used to characterize the as-synthesized MWCNTs. Thermogram pattern for acid functionalized MWCNTs (data not shown) has significantly difference in mass loss as compared to the as-synthesized MWCNTs. As from thermogram observation, the onset temperature of acid functionalized MWCNTs combustion is lower than onset temperature of as-synthesized MWCNTs. This might be due to the more oxygenated groups being generated on the carbon nanotubes surface during the functionalization process [14]. The oxygenated groups were more reactive towards oxygen, which made the sample combusted earlier at lower temperature. The TGA results obtained also confirm the persistent of the structural form of MWCNTs as the high percentage of the carbon decomposition in the functionalization MWCNTs, showing that not much of the defects occurred thus maintaining the thermal stability of this material towards high temperature. Table 1.0 showed the percentage of the mass loss composition taken place in the as-synthesized and functionalized MWCNTs.

Table 1.0: Mass loss composition in MWCNTs

| Sample    | Weight loss (%)       |                       |
|-----------|-----------------------|-----------------------|
|           | As-synthesized MWCNTs | Functionalized MWCNTs |
| 100 °C    | 4%                    | 9%                    |
| 100-550°C | 5%                    | 23%                   |
| 550-900°C | 91%                   | 68%                   |

The structural and morphology study of MWCNTs has been analysed by FE-SEM. Figure 3.0 shows the effect on the surface of the nanotubes before and after acid treatment. From FE-SEM micrograph of as-synthesized and functionalized MWCNTs, there has shown a significant different on the nanotubes structure affected by the aqueous acid functionalization process. The smooth surface of the nanotubes has been altered to appear as groovy surface after the functionalization process, which can be associated to the chemical functional groups attached on

the nanotubes surface. The transparency of nanotubes also has been decreased after the functionalization as compared to the as-synthesized MWCNTs which possibly related the introducing of functional groups [15, 16].

From the FE-SEM micrograph of acid treated MWCNTs samples, it can be seen that there is no MWCNTs structural damaged occurred, regarding of tubes shortening by the acidic oxidation process. It is probably due to the mild condition of aqueous acid solution as compared to the concentrated acid which caused severe structural damage to the nanotubes structure through tubes scission as been reported by Goyanes *et al* (2007) [10].

Further MWCNTs morphology characterization was conducted using TEM analysis. Figure 4.0 shows the TEM micrograph of as-synthesized and functionalized MWCNTs. From the micrograph, the morphology of the functionalized MWCNTs observed was complemented with the FE-SEM micrograph. The long and straight tubular of as-synthesized MWCNTs floss has transformed to twisted tubular MWCNTs floss after acid treatment. The fragmented surface of the sidewall acid functionalized MWCNTs was resulted by the ultasonication applied during the functionalization process.

The mild acid mixture used in this study was effectively did not attacked open the tube, while it is strong enough to attack the nanotube walls and generate functional groups. It also can be seen throughout of the morphology structure of acid functionalized MWCNTs. The dispersion test was conducted to determine the dispersion capability of acid functionalized MWCNTs using this method.

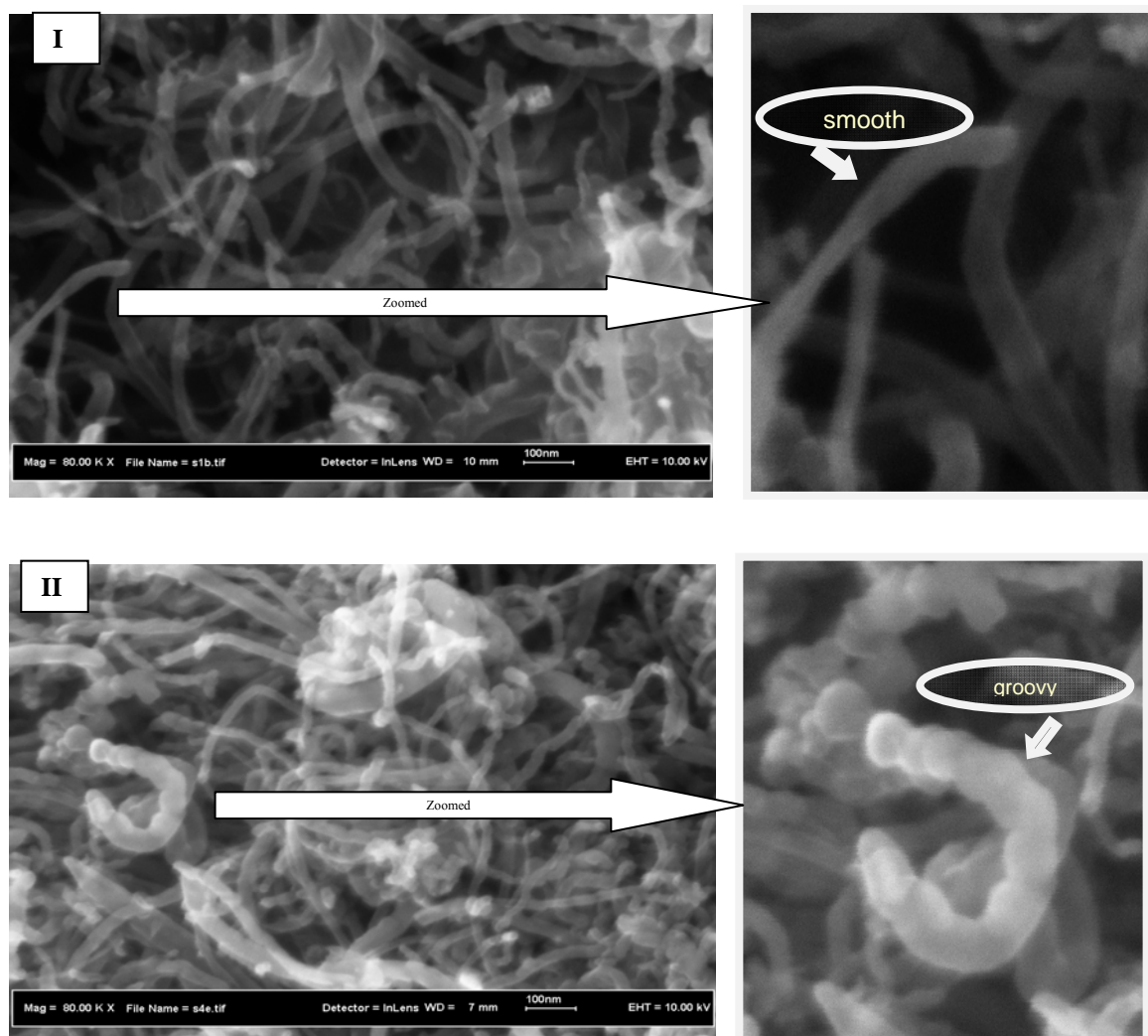


Fig. 3.0: FE-SEM micrograph for as-synthesized (I) and functionalized MWCNTs (II)



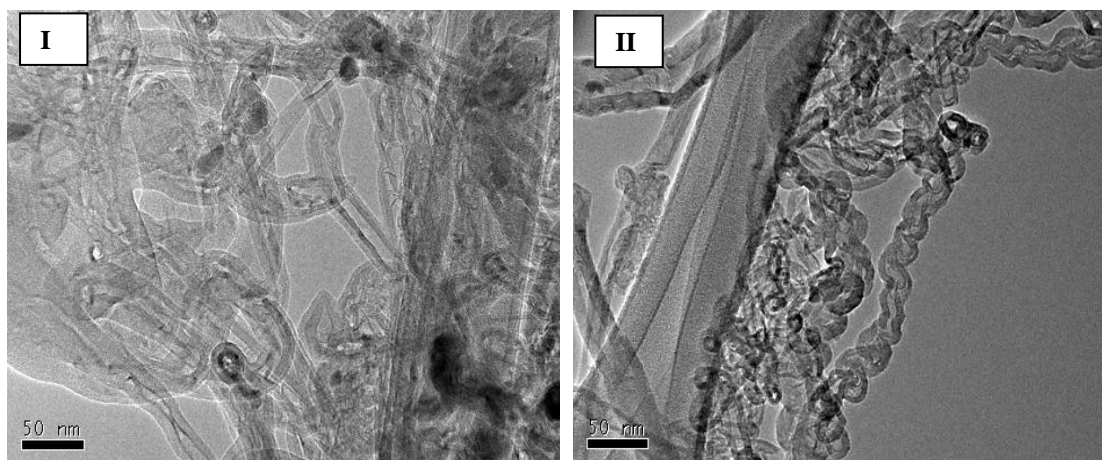


Fig. 4.0: TEM micrograph for as-synthesized (I) and functionalized MWCNTs (II)

### 3.2 Dispersion Test

The dispersion test of as-synthesized and acid functionalized MWCNTs was tested by the dispersion of a small amount of each MWCNTs samples in acetone using the water bath ultrasonic for 5 minutes [17]. From the observation (Figure 5.0), it shows that the functionalized MWCNTs remained as stable suspension in the acetone for more than 20 days as compared to the as-synthesized MWCNTs, which give unstable suspension after 5 hours.

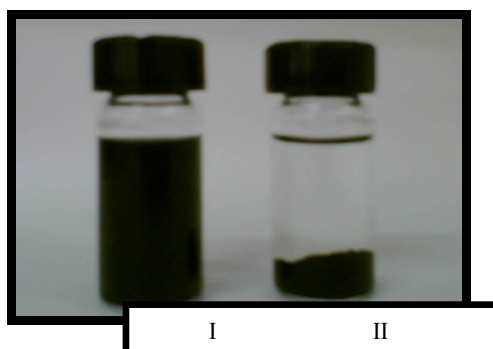


Fig. 5.0: Photograph of MWCNTs in acetone (I) functionalized MWCNTs (II) As-synthesized MWCNTs

As the results shows from the dispersion test of MWCNTs in acetone, stable colloidal form of functionalized MWCNTs dispersion is feasible to obtain due to the presence of functional groups on the surface of the carbon nanotubes. The weak tube-tube interactions among the MWCNTs floss after the debundling process, as well as their enhanced polarity by the carboxylation on MWCNTs has improved functionalized MWCNTs dispersibility and subsequently, stabilized the MWCNTs suspensions. It is explained by the carbonyl (C=O) in acetone which is polar in nature, formed the hydrogen bond with the carboxylated functional groups of MWCNTs outer-wall surface. On the other hands, the sonication technique applies during the functionalization, as well as in the dispersion process also gave energetic effect in getting the MWCNTs bundles to start loose. Compared to the heat treatment such as refluxing

technique, the ultrasonic wave produce through the water vibration has effectively hindered the disruption on MWCNTs structure, yet stabilized the MWCNTs colloidal in aqueous media.

#### 4. Conclusion

MWCNTs functionalized with carboxyl groups were obtained through treating MWCNTs with mixture of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> aqueous acid solution in mild concentrations. Well dispersed MWCNTs were obtained after acid functionalization due to the generated of the OH and COOH groups that were functionalized to the surface of the carbon nanotubes. The presences of functional groups on the outer-wall of MWCNTs were successfully form hydrogen bonds with acetone molecule when dispersed in acetone. The advantages of sonication method is the simply and easy way for the functionalization of MWCNTs in the aqueous acid solution without severe structure destruction of MWCNTs. Furthermore, stable colloidal system of functionalized MWCNTs has achieved, thus confirmed the effectiveness of this method to disperse MWCNTs.

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