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Mechanochemical Synthesis of CNT/ZnO Hybrid Materials

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Abstract: A study on the synthesis of multiwalled carbon nanotubes (MWCNT) and zinc oxide (ZnO) hybrid materials using the mecahnochemical technique has been conducted. MWCNT was dispersed in sodium dodecyl sulfate (SDS) solution. ZnO was formed at milling time of 2, 5 and 10 hours. The XRD results showed only small peaks of ZnO. This suggests that at longer milling time, the ZnO crystals were either become amorphous or have reduced in sized so as not to be detected using XRD. ZnO has also been doped with Manganese (Mn) which have affected the crystal structure and surface morphology of the sample. In summary, we have demonstrated a simple and efficient technique for producing CNT/ZnO hybrid materials that may have enhanced applications as chemical sensors, fuel cell electrodes and piezoelectric generators.

Introduction

Over the past decades, carbon nanotubes have attracted interest in fundamental and applied research due to their unique properties in electronics, mechanics, thermals, photonics and catalytic properties [1,6]. Due to these exceptional qualities and characteristics CNTs provide the potential in various applications such electrochemical devices, and carbon based nanoelectronics [1,4]. Zinc oxides is an important semiconductor material with a wide band gap of 3.37 eV have an interesting properties such as optical, electronic, chemical and mechanical properties [1,8,9]. ZnO nanostructures offer great applications potentials for various electronics and optoelctronic devices [7,8,10]. The previous study reported that doped ZnO thin films can enrich its optical and electrical properties [7,10,11]. CNT/ZnO hybrids have been shown to enhanced the applications of CNTs as chemical sensors [12] and electrodes materials [13]. The most common method of incorporating ZnO into CNTs was by the sol gel technique [14], which lack reproducibility.

In this paper we report a simple technique for the synthesis of CNT/ZnO and CNT/ZnO:Mn hybrid materials by the mechanochemical method. The dispersion of CNT in SDS solution and the formation of ZnO from zinc acetate were conducted using the ball milling technique.

Experimental

To synthesis the hybrid materials, zinc acetate was used as the source for zinc and hexamethylenetetramine (HMTA) as the reducing agent. For doped MWCNT/ZnO, manganese nitrate was used. 20 ml MWCNT/SDS solution containing 0.2 mg CNT and SDS each was mixed with 0.5 g zinc acetate and 0.5 g HMTA for pure ZnO/CNT and 0.5 g $MnNO_3$ was added for Mn doped ZnO. Samples were ball milled using the Fritsch Pulverisette 7 at 500 rpm for 2, 5 and 10 hours. The samples were then rinsed thoroughly in de-ionized (DI) water and characterized using Scannning Electron Microscopy (SEM) and x-ray diffraction using a probe beam at wavelength of 1.540600 Å.

Results and discussion

The results of the analysis of CNTs, CNT/ZnO and CNT/ZnO: Mn (doped) is presents. The samples are characterized by SEM and XRD. The effect milling time will be analyzed. Also, comparison of the existence of the composites on sample such as the manganese doped zinc oxide will be investigated. Fig. 1 shows the SEM micrographs of CNT/ZnO composite ballmilled for different time with magnification of 5K. There is no CNTs on the sample surface observed in Fig. 1 (a) with imperfections on the sample surface of CNT/ZnO after 2 hours mechanical milling .This is because the milling time is low by the assumption that samples are not synthesized yet. When the milling time is increased to 5 hours as shown in Fig. 1 (b), the morphology of CNT/ZnO shows a growth of CNTs at certain place with agglomerated nanoparticles. After the sample was milling for 10 hours, Fig. 1 (c) shows that CNTs appeared at all surface.

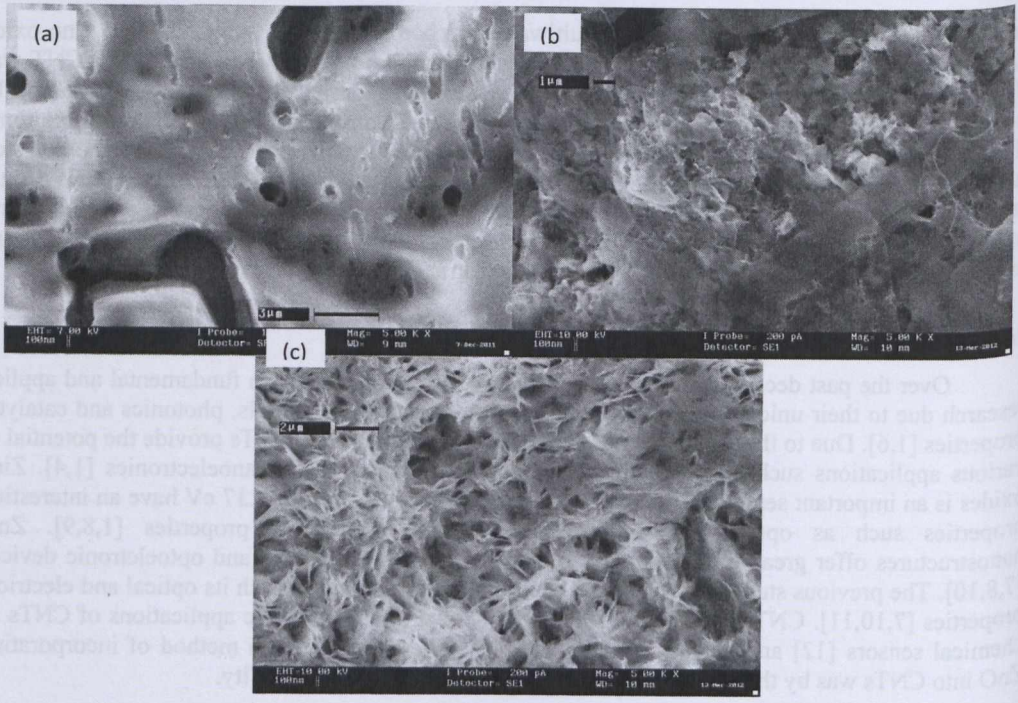

Fig. 1. SEM micrographs with scale of 5K magnification of CNT/ZnO composite ballmilled for (a) 2 hour (b) 5 hours (c) 10 hours .

Fig. 2 represents the manganese doped ZnO carbon nanotubes for three different milling time, 2 , 5, and 10 hours . Fig. 2 (a) shows the CNT/ZnO are initially on the entire surface which

similar to Fig. 1 (c) . This reveals that the sample are not synthesis yet , and no reaction of doping is observed. When the milling time increased to 5 hours as in Fig. 2 (b), the CNT/ZnO :Mn(doped) growth showed the sample are being synthesis and react with Mn doped . SEM micrograph reveals that the diameter of the CNTs also reduces when the milling time has increased to 10 hours as shown in Fig. 2 (c) and the average crystallize size were reduced as compared to Fig. 2 (b) which similar to XRD analysis [11]. By comparing the undoped and doped of CNT/ZnO, crystalline structure is observed with many changes where CNTs behavior already appeared at low milling time as analyze in XRD [7, 10].

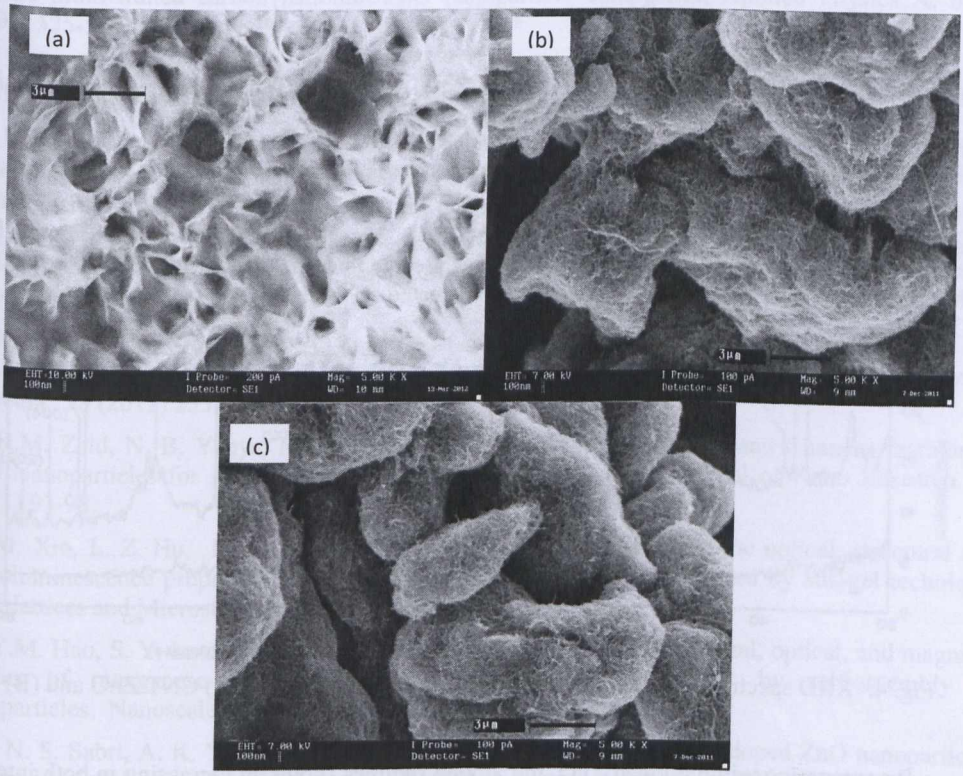

Fig. 2. SEM micrographs with scale of 5K magnification of CNT/ZnO:Mn doped composite ballmilled for (a) 2 hour (b) 5hours (c) 10 hours.

To observe the crystalline mechanism of ZnO and ZnO:Mn (doped) carbon nanotubes the XRD analysis were studied. This study focuses on the effect of milling to the crystalline mechanism of the composites. Fig. 3 shows the XRD pattern of (A) pure MWCNTs , (B) CNT/ZnO, and (C) CNT/ZnO:Mn (doped) composites ballmilled for 2 hours. The XRD pattern for CNT/ZnO:Mn (doped) composites as in Fig. 3 shows diffraction peaks at $2\theta = 56$ which correspond to (110) of zinc oxide (ZnO). On the other hand, no diffraction peak of ZnO observed for CNT/ZnO as in Fig. 3. However, at angle $2\theta = 25$ correspond to (002) of carbon-25 was observed in CNT/ZnO:Mn (doped) composites. The presence of manganese ions also influence the broadening of peak for doped sample [5,8]. This effect has been observed that Mn succesfully be a feature of ZnO (002), (101), (102), (110), (103), (201) and (202) planes in Fig. 3 as expected from previous studies of ZnO structure [7,10,11].

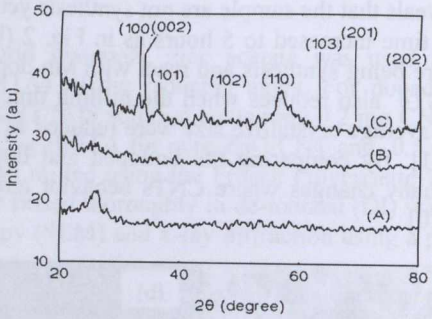

Fig. 3. XRD spectra for (A) MWCNTs, (B) CNT/ZnO, and (C) CNT/ZnO:Mn(doped) composites ballmilled for 2 hour.

Fig. 4 shows the XRD spectra for CNT/ZnO and CNT/ manganese doped ZnO composites ballmilled 5 hours and 10 hours. It been observed in Fig. 4 (a) the peak point of the triangular for CNT/ZnO:Mn (doped) with diffraction angle at $2\theta = 32, 56$ correspond to (100) and (110), resectively. This planes also known as the (10) band. Beside that, the diffraction peak plane of (002) with diffraction angle $2\theta = 25$ for carbon are detected in both Fig. 4 (a) and (b) for CNT/ ZnO:Mn(doped).

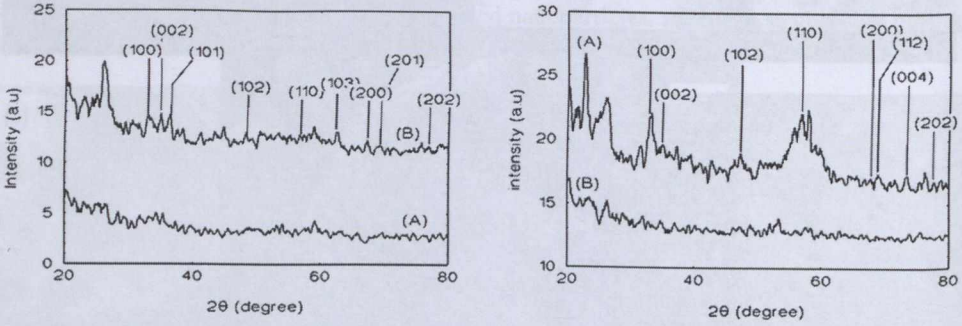

Fig. 4. XRD spectra of (a) 5 hours and (b) 10 hours ballmilled of (A) CNT/ZnO and (B) CNT/ZnO:Mn(doped) composites.

By comparing with undoped ZnO, the doped samples shows an increasing in both intensity and full width at half maximum (FWHM) as shown in Fig. 3, Fig. 4 (a) and 4 (b), respectively. The contents of doping of Mn seems to have influence the crystallite structure of the ZnO as reported by other researcher [3,5,7]. However, after milling time have increased, the diffraction peak become narrow as shown in Fig. 4 (a) and (b), respectively. The increasing of chemical milling exhibit decreasing in crystallites size and the grain size of the sample. It have been report that crystal structure of ZnO depends on the milling time as well [2,11].

Conclusion

Mechanochemical Synthesis of Cnt/ZnO Hybrid Materials was succefully done by produced two composites, CNT/ZnO and CNT/ZnO: Mn (doped). The effect of ball milling time based on XRD analysis showed that ZnO was formed at milling time between 2 and 5 hours. At 10 hours milling time the XRD results showed little ZnO peaks. Only carbon present in the XRD peak. This suggests that at longer milling time, the ZnO crystals were either become amorphous or have reduced in sized so as not to be detected using XRD. Beside that, the doping of Mn seems have affected the size of sample when the milling time increase. It can be concluded that the samples were influence by Mn doped in both crystallize structure and surface morphology.

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