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ENHANCEMENT OF GIANT MAGNETORESISTANCE IN Fe_2O_3-MWCNT/PVA NANOCOMPOSITE FILM

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ABSTRACT

ENHANCEMENT OF GIANT MAGNETORESISTANCE IN Fe_2O_3-MWCNT/PVA NANOCOMPOSITE FILM. Synthesis and magnetic properties characterization of Fe_2O_3-MWCNT/PVA nanocomposite film were carried out. Fe_2O_3-MWCNT as a filler of nanocomposite thin film were synthesized using simple mixing methods from a solution containing $FeCl_3$, and Multi-Walled Carbon Nanotube (MWNT). The solution was sonicated for almost 20 minutes then dried at 450 °C for one hour. The mixture of the two composition was dispersed with Sodium Dodecyl Sulfate (SDS) in 20 mL aquabidest and homogenized by ultrasonicator for 15 minutes at 40 °C. Then filler was then mixed with Polyvinyl Alcohol (PVA) with some various concentration and dried overnight at room temperature. X-Ray Diffraction (XRD) analysis and Raman Spectroscopy were used to find out the presence of Fe_2O_3 phase in as prepared sample. Iron oxide phase partially filled in the wall of MWCNT observed by Transmission Electron Microscope (TEM). The Giant Magnetoresistance (GMR) properties were investigated. The maximum GMR value was negative 80% of the composition 1:9 filler/matrix volume ratio. The linear negative of the magnetoresistance (MR) ratio is coincident with a model as proposed by Nguyen, Spivak and Shklovskii (NSS) and related to the effect of quantum interference between Fe_2O_3-MWCNT in PVA matrix.

***Keywords*:** Magnetoresistance, Nanocomposite film, Fe_2O_3-MWCNT, Polyvinyl Alcohol

ABSTRAK

PENINGKATAN SIFAT *GIANT MAGNETORESISTANCE* PADA LAPISAN TIPIS NANO KOMPOSIT Fe_2O_3-MWCNT/PVA. Sintesis dan karakterisasi sifat magnetik pada bahan nanokomposit film Fe_2O_3-MWCNT/PVA telah dilakukan. Bahan Fe_2O_3-MWCNT sebagai pengisi pada nanokomposit film disintesis dengan metode pencampuran sederhana dalam suatu larutan yang mengandung $FeCl_3$ dan MWCNT. Kemudian larutan disonikasi selama 20 menit lalu dikeringkan pada suhu 450 °C selama 1 (satu) jam. Kemudian campuran ini didispersi dengan larutan *Sodium Dodecyl Sulfate* (*SDS*) dalam 20 mL *aquabidest* dan dihomogenisasi dengan ultrasonik selama 15 menit pada suhu 40 °C. Lalu campuran *filler* ini dicampurkan dengan *Polyvinyl Alcohol* (*PVA*) untuk beberapa konsenstrasi dan dikeringkan selama satu malam sehingga terbentuk film. Analisis fasa dengan *X-Ray Diffraction* (*XRD*) dan Raman spektroskopi pada cuplikan sebelum menjadi film telah dilakukan. Ditemukan adanya fasa Fe_2O_3 dan MWCNT. Pengamatan dengan *Transmission Electron Microscope* (*TEM*) menunjukkan adanya sebagian partikel Fe_2O_3 yang masuk ke dalam dinding dan tabung MWCNT. Sifat *magnetoresistance* (*GMR*) bahan telah diukur pada cuplikan film. Terukur nilai nisbah *GMR* sebesar negatif 80% pada film dengan komposisi perbandingan volume *filler*/matriks sebesar 1:9. Karakter linier negatif pada nisbah *Magnetoresistance* bersesuaian dengan model yang diusulkan oleh *Nguyen*, *Spivak* dan *Shklovskii* (*NSS*) terkait dengan efek interferensi antara Fe_2O_3-MWCNT di dalam matriks *PVA*.

Kata kunci: *Giant Magnetoresistance*, *Nano composite film*, Fe_2O_3-MWCNT, *Polyvinyl Alcohol*

INTRODUCTION

Carbon nanotubes (CNTs) are carbon nano-structures that have one or more walls, with nanometer-scale diameters. There are several types of CNTs, including the single - CNT or SWCNT, Double CNT or DWCNT and Multi-Walled CNT or MWCNT. Such materials have excellent mechanical and chemical prop-erties of cells tube either in the open or closed state without losing its stability. Various techniques of filling CNTs with metal materials, biomolecules, salts, organic materials have been carried out. Filling proce-dure could be performed during the synthesis, or by filling CNTs that followed the opening portion. For charging with metal materials are usually Fe, Ni and Co[1,2].

Recently, magnetic carbon nanotube compo-sites were obtained by filling carbon nanotubes with paramagnetic iron oxide particles. Measurements indicate that these functionalized nanotubes are superparamagnetic at room temperature[3].

Since the magnetoresistance or magneto conductance film have potential application as printable magnetic devices [4]. Therefore, it is interesting to study the metal-filled MWCNT, the magnetoresistance properties of composite materials in the form of thin film combined with polymer[5]. The aims of this research is to increase the magnetoresistance (MR) properties of nanocomposite films of Fe_2O_3-MWNT/PVA, where the precursor synthesis is using $FeCl_3$ and MWCNT, in order to utilize the concave inner character for charg-ing the iron oxide into MWCNT. This is different from previous research reports about the magnetoresistance properties of PVA matrix containing iron-oxide only. The precursors used in those work were $FeCl_2$ and $FeCl_3$ without containing MWCNT [6].

EXPERIMENTAL METHOD

Iron Oxide Filling MWCNT

Multi-Walled Carbon Nanotube (MWNT) used in this work were produced by catalytic chemical vapor deposition (CCVD) from Nanostructured & Amorphous Materials, Inc. USA. The MWNT have purity of 95%+, inner diameter of 5- 10 nm and length of 10 - 30 µm. An amount of MWNT were added with aquadest then sonicated for 20 minutes. MWNT solution, was then transferred to a beaker glass con-taining, over-saturated of iron (III) chloride ($FeCl_3$). As prepared solution was then stirred for 10 hours at room temperature.

The next important step is quick-washing and multicentrifugation. Quick-washing was performed by using concentrated HCl to wash out $FeCl_3$, which is not incorporated into the nanotube, then followed by multi centrifugation using aquadest, where the water was removed and replaced in each cycle. At the last step, the sample was purified by an-nealing of 450°C in air for one hour to decompose $FeCl_3$.

Composite Film

The composite films were prepared by simply mixing Fe_2O_3-MWCNT dispersed in SDS with 10% PVA solution for 4 variation of concentration with a total volume of 5 ml. The solution was then poured into a petry dishes to dry naturally overnight. Charac-terization of the samples were performed at the Ad-vanced Materials Laboratory of PSBTM - BATAN by using Raman spectroscopy and XRD to determine phase in the sample, Vibrating Sample Magnetometer (VSM) for the MH curve and Four Point probe for MR. Observations of nanostructure precursor of iron-filled MWCNT was performed by using TEM at Gadjah Mada University.

RESULTS AND DISCUSSION

Phase Determination

Determination of the precursor phase was performed by using Raman spectroscopy technique with results as shown below. Figure 1 shows that the peaks at 221, 286, 406, 502, 602 cm-1 indicates the presence of α-Fe_2O_3 phase [7], while the peaks of the D-band and G-band in 1309 and 1567 and 1608 cm-1 are the peak of

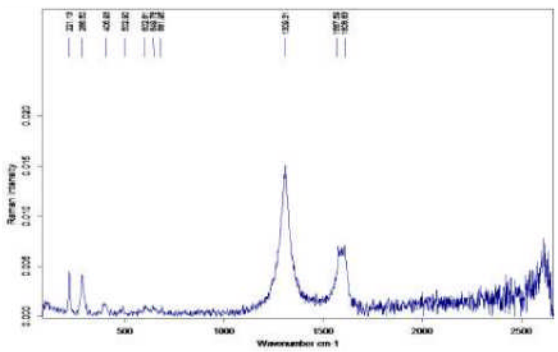

Figure 1. Raman spectrum of sample Fe_2O_3-MWCNT post heated at 450 ºC

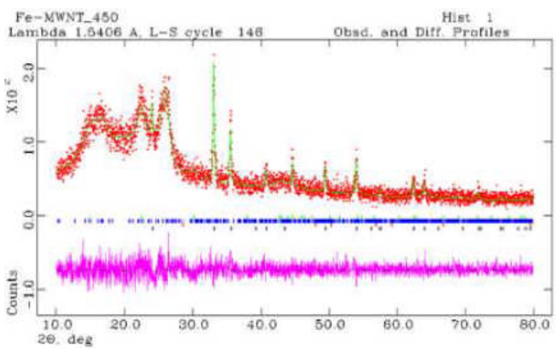

Figure 2. Refinement patterns of XRD data of Fe_2O_3-MWCNT (450 ºC)

Table 1. Phase Determination in sample Fe_2O_3-MWCNT (450 ºC)

Name of Compound	Phase	Mass Fraction (% wt.)
Graphite-2H	C (Hexagonal-186)	30.03
Carbon	C (Orthorombic-19)	38.23
Graphite	C (Hexagonal-166)	18.72
Iron Oxide	Fe_2O_3	12.42
Iron	Fe	0.60

MWCNT [8]. Figure 2 shows the XRD pattern of precursor Fe-MWCNT after heating at 450 °C. Analysis result as shown in Table 1 confirmed the existence of the phases present in the sample after heating Fe_2O_3-MWCNT at 450 °C.

The mass fraction of α-Fe_2O_3 phase was 12.42% and hexagonal-phased carbon as a major constituent of MWCNT has turned into a hexagonal-186 and hexagonal-166 phased carbon with each fraction was 30.03% and 18.72%, respectively.

Magnetization Curve

Measurement of M-H magnetization curve was performed by using VSM at Advanced Material Laboratory PSTBM. M-H magnetization curve in Figure 3 show that it has ferromagnetic properties with Ms = 0.3 emu g-1 in the external field H = 1 Tesla (10kOe). However, the curve shows the existence of hysteresis indicating the presence of ferromagnetic spin ordering of α-Fe_2O_3 nanoparticles. The presence of Fe nanoparticles trapped in the CNT will bring hysteresis on the measurement results of the M-H curve[9].

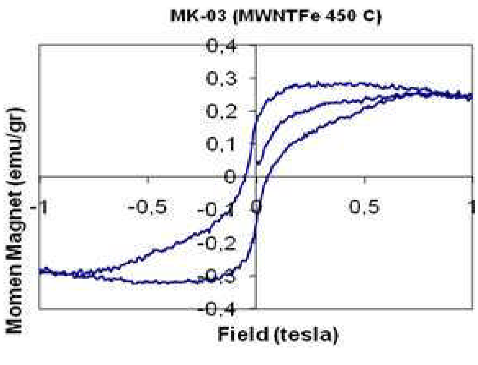

Figure 3. Magnetization curve M-H of precursor Fe_2O_3-MWCNT post heat treatment 450 °C

Nanostructure by Transmission Electron Microscope

Observation of nanostructures on the sample was performed by using Transmission Electron Mi croscope (TEM) at Gadjah Mada University. The observation condition are 800,000 times for magnification at a voltage of 120kV. Figure 4 shows that the phase of Fe_2O_3 (represented by black color) could enter the nanotube with the inner diameter of about 20 nm and the outer diameter of about 50 nm. The phase of Fe_2O_3 was impregnated not only through the hollow tube but also through the damaged all of MWCNT when interacting with nitric acid. The inclusion of this phase into MWCNT through hollow capillary is due to the nature of MWCNT during the mixing process takes place. The opened cap of MWCNT used in this study allowed the entry of Fe_2O_3 at 400 ºC. This result is slightly different from the techniques developed by Valinejad et.al [10] by heating the MWCNT at the tem-perature of 700 ºC and 810 ºC, which generate much less the percent loss of material MWCNT.

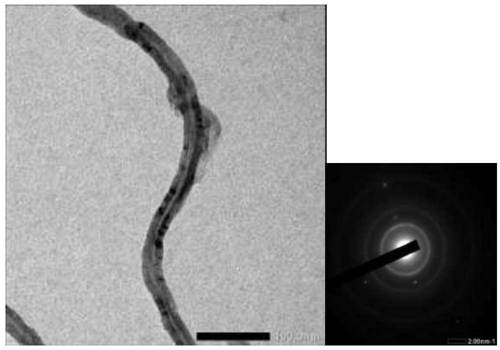

Figure 4. TEM image and SAD from the iron oxide-MWCNT sample at 800.000 x exposure and Voltage = 120kV. Length of bar is 100 nm

Magnetoresistance of the Film

MR is defined as the difference between the value of resistance of materials in zero magnetic and maximum magnetic field. It can be written as Equation (1):

$$\frac{(R_0 - R_H)}{R_H} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where H = 0.8 Tesla (T). MR ratio measurement was conducted by using the Four Point probe (FPP). The results of measurements of the MR ratio on the system of Fe_2O_3-MWCNT/PVA thin film on top of Si (100) with volume ratio filler/matrix of 1: 9 shows that the linear MR ratio is -80% at 0.8 Tesla magnetic field (or 8kOe), as shown as Figure 5.

This result is higher than the phenom-enon of magnetoresistance (MR) in iron oxide / PVA film as reported elsewhere [6] where MR ratio is -10% in the field H = 10kOe. The phenomenon of MR, which occurs in both types of systems is due to a change in the spin ordering of Fe nanoparticle under the influence of an external magnetic field in the system of Fe_2O_3-MWCNT or transformation of nanoparticle of α-Fe_2O_3 to α-Fe_2O_3-MWCNT system. The characteristic of linear negative magnetoresistance (MR) in this system were coincident with the prediction model for Variable Hopping Transport (VRH) with external field at low magnetic field due to the effect of quantum inter-ference between extended states (larger localization lengths) as observed in CNT film [11].

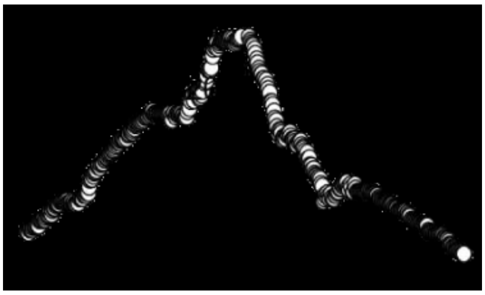

Figure 5. A typical magnetoresistance ratio in film composite of Fe_2O_3-MWCNT/PVA (1:9 v/v ratio)

Table 2. The ratio of magneto resistance for Fe_2O_3-MWCNT/PVA film

Sample code	Volume ratio Filler/matrix (v/v %)	Weight ratio (wt%)	MR ratio (%) At H= 8 kOe
L1-F	1 : 19	0.24	-68
L2-F	1 : 9	0.56	-80
L3-F	1 : 4	1.14	-52
L4-F	1 : 1	4.56	-14

Also this phe-nomenon has been observed in carbon based mate-rials[12]. This phenomenon was slightly different with the result of magneto conductivity in PVA-MWCNT composites only as reported by Chakraborty et.al [13]. But quite similar with the result of magnetoresistance in magnetite-Polypyrrole metacomposites as reported by Jiang Guo et.al [14] and magnetoresistance in polyaniline composites [15,16]. Table 2 shows the summary of Magnetoresistance measurement for Fe_2O_3-MWCNT as a filler and PVA film as a matrix.

CONCLUSION

Nanocomposite thin film α-Fe_2O_3-MWCNT/ Polyvinyl Alcohol (PVA) were successfully synthesized by sim-ple mixing method. The filling nanoparticles into MWCNT shows α-Fe_2O_3 phase. The highest MR ratio obtained in thin film materials are approximately -80% at Ha = 8kOe with a high degree of linearity. The linear negative of the MR ratio is coincident with a prediction model as proposed by NSS and related to the issue of quantum interference between α-Fe_2O_3-MWCNT.

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