MSU Fen Bil. Dergi., Cilt 5, Sayı 2, s 465-469 *Araştırma Makalesi/ Research Article*
MSU J. of Sci., Volume 5, Issue 2, p 465-469 DOI : 10.18586/msufbd.347643

# The Investigation of Properties and Production of CNT and BNNT Reinforced ZnO Nanocomposites

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Received (Geliş): 01.09.2017 Revision (Düzeltme):29.10.2019 Accepted (Kabul): 23.11.2017

**ABSTRACT**

Many reinforces have been made to improve the electrical and optical properties of ZnO. There are also nanotubes among these additives. Carbon nanotubes (CNTs) improve the electrical properties of ZnO, but the expected effect on optical properties has not been observed.
In this study, CNTs produced by CVD method and Boron Nitride nanotubes (BNNT) produced by mechanothermal method under laboratory conditions into commercial ZnO were investigated by adding together. For this purpose, CNT 50% wt. and BNNT 50% wt. at two different rates of 0.1% and 1% was added to ZnO. The nanotubes/ZnO powder mixtures produced in this way are compacted and sintered. The electrical and the optical properties of the produced samples with UV-Vis spectrometer were investigated. Electrical conductivity has also been found to increase with the increase in the amount of nanotubes. However, it was observed that the reflectance properties were partially increased.

**Keywords:** Boron nitride nanotube, carbon nanotube, zinc oxide

# KNT ve BNNT Takviyeli ZnO Nanokompozitlerin Üretimi ve Özelliklerinin Araştırılması

**ÖZET**

ZnO'nın elektriksel ve optik özelliklerini geliştirmek adına daha önce pek çok katkılandırma yapılmıştır. Bu katkılar arasında nanotüplerde vardır. Karbon nano tüpler (KNT) ZnO'nun elektriksel özelliğini geliştirirken optik özelliklerinde beklenen etki görülmemiştir.
Bu çalışmada ticari ZnO içerisine laboratuvar şartlarında CVD yöntemi ile üretilen KNT ile mekanotermal yöntem ile üretilen Bor Nitrür nanotüplerin (BNNT) beraber ilave edilerek etkileri araştırılmıştır. Bu amaçla ZnO içerisine ağ. %50'si KNT ve ağ.%50'si BNNT olacak şekilde %0.1 ve %1 gibi iki değişik oranlarda ilave edilmiştir. Bu şekilde üretilen nanokompozit tozlar kompaklanıp, sinterlenmiştir. Üretilen numunelerin elektrik iletkenliği ve UV-vis spektrometre ile optik özellikleri incelenmiştir. Elektrik iletkenliklerinde, nanotüp miktarının artması ile artığı tespit edilmiş. Ancak reflektans özelliklerinde kısmen artış olduğu gözlenmiştir**.**

**Anahtar Kelimeler:** Bor nitrür nanotüp, çinko oksit, karbon nanotüp

## INTRODUCTION

Carbon Nanotubes (CNTs) was discovered by lijiama in 1991 and Boron Nitride Nanotubes (BNNTs) were discovered by Rubio in 1994 [1,2] Like CNTs, BNNTs also have very good mechanical properties due to their tubular structures and $sp^2$ bonds between their layers [3] Single-walled types of CNT contain hexagonal pentagon and hexagonal hexagons. However, BNNTs are flat type formed with four-centred [4] Both materials are produced using similar methods. These methods are arc discharge, arc melting, ball milling and annealing, chemical vapour deposition (CVD), and laser techniques [3, 5]. While CNTs have conductive and semi-conductive character depending on the tube structure, BNNTs are electrical insulating independently from the tube structure [5, 6]. The oxidation stability of BNNT nanotubes is higher than CNTs [7, 8]. BNNTs can be used in the production of new electronic and photo electronic circuits in nanoscale where CNTs are not suitable. Zinc oxide (ZnO) has high strength, good optical properties, chemical stability, and piezoelectric properties as an oxide [9]. ZnO is an n-type semiconductor with a wide band gap (3.37 eV) and its bonding energy is extremely high (60 meV) [10, 11] It can perform band passes by absorbing UV radiation and because of this property, TCO (transparent conductive oxide) can be used as a thin film [12].

Over the last few years, numerous studies have been conducted on nanocomposite synthesis of inorganic materials and carbon nanotubes due to the unique properties of CNTs [13, 14] This is due to the high theoretical electrical conductivity, high aspect ratio, superior thermal conductivity and good mechanical properties of these materials [15]. Synthesis methods of nanocomposites with ceramic matrix are the same with the preparation methods of microcomposites. Conventional powder metallurgy techniques and chemical methods, sol-gel, colloidal and precipitation applications, and template synthesis methods are used [16].

ZnO and CNT couple are promising composite materials for applications in optoelectronic devices [17]. In this study, the changes in optical and electronic properties of nanocomposite with the addition of BNNTs having the similar structure with CNT were examined.

## EXPERIMENTAL

For the production process, synthesis process of CNT and BNNTs to be used as reinforcing member was performed firstly. CVD method was used to synthesise carbon nanotubes. Si substrates were used to deposit on carbon nanotubes. The substrates were washed thoroughly with ethanol and dried in the vacuum oven. The substrates were then placed in a tube furnace. $C_2H_2$ gas (1 l/min) and Ar gas (1 l/min) were passed together through the system at 650 ºC for 1 hour in the furnace. During the furnace cooling, the acetylene flow was interrupted and the argon gas continued to pass through the system. CNTs were synthesized at the end of the process.

BNNTs were synthesized by mechanothermal method. 99.7% pure h-BN powders were used as the starting material. In the study, Fritsch Pulverisette P7 grinding mill and grinding vessel made of hardened steel and grinding balls with 8 mm diameter (100 Cr 4) were used. Grinding was carried out at 850 rpm, BPR 32/1 for 5 hours under Ar atmosphere. Catalyst powder was added at the last stage of the grinding process. As the catalyst, NiO (Sigma-Aldrich) was added in 4 wt.%. At the end of grinding process, the powders were transferred to Al boats and placed in a tube furnace for annealing process. The samples were subjected to heat treatment at 1300°C for 2 hours under Ar+$NH_3$ gas flow (0.2+0.5 lt/min ) and BNNTs were synthesized at the end of the process.

The produced nano-reinforcements were kept in a mixture of nitric acid (Sigma-Aldrich) and hydrochloric acid (Sigma-Aldrich) for 3 hours for purification process. The powders were then washed several times with distilled water and dried in an oven at 150 °C for 10 hours. Nano-reinforcements were added to 100 ml of ethanol and mixed for 2 hours using ultrasonic homogenizer to make a good distribution within the structure. Sufficient amount of ZnO (99.7) powder was added to the obtained mixture and subjected to an ultrasonic bath at 80 °C. As a result, nanotube powders in two different rates such as 0.1% and 1% were mixed with ZnO so that 50 wt.% would be CNT and the other 50 wt.% would be BNNT. The composite powders were pressed at 600 MPa using a 14-mm die. The obtained compacted samples were sintered for 2 hours at 600 ºC (Furnace was heated at 10 ºC/min). Sintering process was performed under Ar atmosphere. During sintering, this gas flows at the rate of 2 (l/min) from the system.

SEM examinations of the samples were carried out on a JEOL JSM-7001F brand electron microscope. The electrical conductivity of the composites was measured by using double probe method with Keithley 6517A Electrometer/High-Resistance Meter device. Optical measurements of the samples were performed by using Shimadzu UV-3600 PC UV-VIS spectrophotometer device.

## RESULT and DISCUSSION

SEM examinations of the produced nanocomposite in Figure 1 show that nanotube mixture was dispersed in ZnO. There was no structural difference between CNT and BNNT under the electron microscope. However, BNNTs formed as thicker and longer tubes compared to CNTs since they have different production methods. The diameters of the nanotubes were in a quite wide distribution range. Their lengths were in several μm levels. Figures 1.a and b show that their distributions also had limitations along with the increase in nanotube amounts. Nanotubes are seen as a net on the surfaces of ZnO particles.

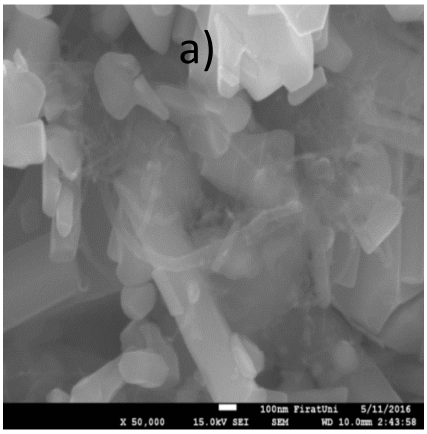
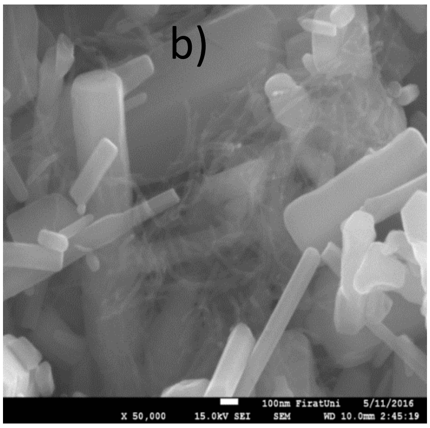



**Figure 1.** a) SEM image of 0.1% CNT-BNNT




b) SEM image of 1% CNT-BNNT reinforced ZnO composites

Ionic conductivity in ceramics is formed by the transfer of ions (positively or negatively charged atoms) from one region to another via point defects called as voids in the crystal lattice. While a small amount of ion jumping occurs at normal ambient temperatures, voids start to move at high temperatures, and some ceramics act as fast-ionic conductors [18]. Figure 2 shows the electrical conductivities of CNT-BNNT-reinforced ZnO composites depending on the temperature. Development of conductivity property in CNTs showing conductive or semiconductive characteristics depending on the semiconductor ZnO and tube structure is an expected situation. However, as is seen in Figure 2, it was found that the addition of BNNTs into the structure did not develop the electrical conductivity of CNT-BNNT reinforcement compared to pure ZnO. This is because BNNT is an electrical insulator. Increased nanotube amount provides some increase in electrical conductivity.

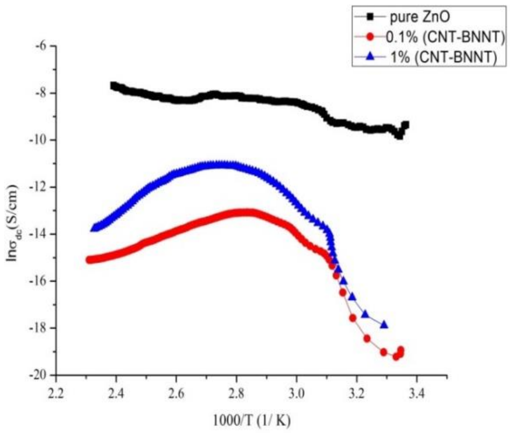



**Figure2.** Plots of the electrical conductivity versus temperature of the ZnO/CNT-BNNT nanocomposites

When the conductivities at room temperatures were examined, the conductivity of pure ZnO was higher than 60%. In addition, electrical conductivities of 0.1% and 1% reinforced samples were very close to each other at room temperature. As the temperature increased, the electrical conductivity of both 0.1% and 1% samples increased significantly. At 370 K, electrical conductivity of both 0.1% and 1% samples reached to a maximum value. As the temperature increased further, the electrical conductivity of both samples decreased. But at the same temperature increase, the conductivity values of pure ZnO increased at every temperature. The mentioned increase amount was in lower rates. CNT rate of the sample containing 1% CNT-BNNT was 0.5%. It was found in previous studies that addition of 0.5% CNT into ZnO increases the conductivity very significantly [19].However, even though there was 0.5% CNT in ZnO in this study, it did not affect the conductivity at the expected level compared to pure ZnO. This is thought to be associated with the presence of 0.5% BNNT in the sample.

The diffuse reflection theory was developed on scattering surfaces by Kubelka-Munk in 1931. The Kubelka-Munk model is the relationship between the intensity of the measured infrared and the sample concentration.

Kubelka -Munk function;

$$F(R) = \frac{(1-R)^2}{2R} \tag{1}$$

Here, F (R) is the Kubelka-Munk function corresponding to the absorbance and R is the reflection. The Kubelka-Munk function is used for this. As a result, the relationship used to determine the optical band gaps of conventional semiconductors is as follows [19].

$$F(R)h\nu = A(h\nu - E_g)^n \tag{2}$$

In Figure 3, a sharp increase above 400 nm is seen in reflectance values for pure ZnO and composite samples. When the composite samples were compared with pure ZnO, it was also observed that the reflectance values decreased. As expected, the increase in the amount of CNT in the samples caused the decrease in the reflectance values. This is a result compatible with previous studies. 1% reflectance values in this study were close to those performed previously and those obtained from the samples in which 0.5% CNT was added into ZnO [19].

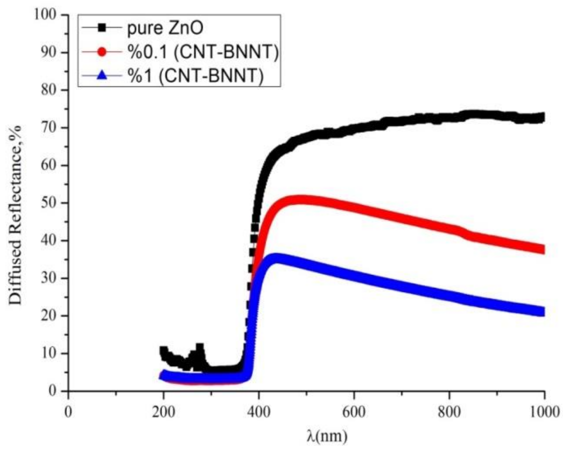



**Figure3.** The reflection spectrum of ZnO/CNT-BNNT nanocomposites

Figure 4 shows Plots of $(F(R)hv)^2$ versus the photon energy ($hv$) of the ZnO/CNT-BNNT nanocomposites. As is seen, bandwidth Eg value of pure ZnO was about 3.23 eV of pure ZnO. It was 3.2 eV, interestingly the same in the samples containing 0.1% and 1% CNT-BNNT. Even though there was a CNT-BNNT difference with 10-fold amount between these two samples, bandwidth of these two samples was found to be the same. In the previous studies, there was no change in the bandwidth of ZnO even with 0.1%, 0.5% and 1% CNT reinforcement to ZnO and it was found to be almost identical to ZnO [19]. In this study, however, the amount of BNNT caused this value to decrease even slightly. However, even though there was a 5-fold difference in the amount of BNNT between two samples, the reason behind why the band energy range was the same was evaluated as follows; while there was a decrease in the band energy range up to a certain BNNT rate, BNNT level over this rate did not cause any change.

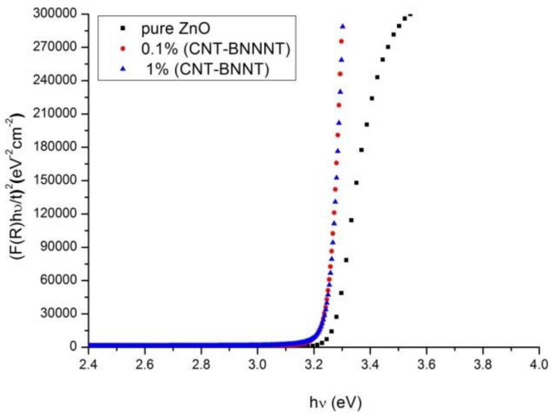



**Figure.4:** Plots of $(F(R)hv)^2$ versus the photon energy ($hv$) of the ZnO/CNT-BNNT nanocomposites.

## CONCLUSION

CNT and BNNT were added together into the semiconductor ZnO as reinforcements and the nanocomposites were successfully produced. In the study, it was seen that reinforcing elements did not develop the electrical properties of ZnO. However, increasing the amount of nanotubes increased the electrical conductivity slightly. It was observed that reflectance values of the samples decreased with the increased nanotube amount and the bandwidth was lower than ZnO and it did not change with the increased nanotube ratio.

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