Rapid Microwave-Assisted Synthesis of Nickel Oxide/Multi-walled Carbon Nanotube Composites

Prasopporn Junlabhut[1*], Chatpong Bangbai[2] and Chokchai Kahattha[3]

[1]*Department of Applied Physics, Faculty of Science and Technology, Rajabhat Rajanagarindra University, Chachoengsao 24000 Thailand*
[2]*Department of Science and Mathematics, Faculty of Agro-Industrial Technology, Kalasin University, Kalasin 46000 Thailand*
[3]*Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, 680 Nittayo Road, Mueang District, Sakon Nakhon, 47000, Thailand*

Abstract

In this paper, nickel oxide/multi-walled carbon nanotube (NiO/MWCNTs) composites were synthesized by a rapid and simple microwave-assisted method using nickel chloride hexahydrate and UV-treated multi-walled carbon nanotube as a starting precursor. As-synthesized hybrid composite materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR). XRD results indicated that the composites are in form of mixture of two phases of cubic NiO and MWCNTs. SEM and TEM results showed that NiO nanoparticles with average size less than 10 nm were well-decorated on the surface of MWCNTs and the amount of NiO particles increases with increasing irradiation power.

Keywords: Nickel oxide, Carbon nanotubes, Microwave-Assisted method

1. Introduction

In recent years, carbon nanotubes (CNTs) have been greatly attracted attention from scientists and technologists owing to their unique electrical, mechanical, and chemical properties. Up to now, CNTs have been widely utilized as a novel functional material in various kinds of applications including biosensing material [1], supercapacitor [2], field emission device [3] and energy storage [4]. For enhancing their properties, the modification of its surface with metal oxide nanostructures could be a promising technique [5]. Recently, there have been a number of pioneered works focused on the synthesis of nanocomposites of metal oxide/CNTs as potentially applicable materials in optics and electronics [6]. Among metal oxide nanostructures, nickel oxide is recognized as an important functional material in a wide range of applications such as catalyst [7], fuel cell [8], electrochemical battery [9] and magnetic material [10], owing to its distinguished properties including excellent chemical stability, interesting electrical, optical and magnetic properties. According to the distinguished properties of these two materials especially in low-dimensional structures, the integration of CNTs and NiO in form of composites may open a new era of functional materials. More recently, various techniques such as chemical precipitation [11], direct thermal decomposition [12], and chemical vapor deposition [13] have been employed to synthesize NiO/CNT composites with interesting functional properties for practical applications. Nevertheless, these processes require long reaction time and large energy consumption. Many functional materials such as nanocrystalline structures [14], nanoparticles [15], and composite materials [16] have been synthesized by microwave irradiation technique due to its unique advantages such as non-contact, instantaneous and rapid heating rate leading to the minimization of reaction time, and uniformity of heat

Corresponding Author E-mail: pjunlabhut@gmail.com

transfer. In this work, the potential of microwave irradiation is employed to synthesize NiO/MWCNTs nanocomposites via a sol mixture of nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) and MWCNTs. Fundamental properties of as-synthesized composites were investigated and discussed by mean of XRD, SEM and TEM results.

2. Experimental details

Pristine multi-walled carbon nanotubes (MWCNTs) synthesized by infusion chemical vapor deposition were provided by Research Laboratory for Excellence in Nano and Smart Materials, Chiang Mai University, Thailand. The detail of MWCNT synthesis can be found elsewhere [17]. The surfaces of MWCNTs were modified by UV-Ozone treatment method for 60 min to improve their solubility. The treated MWCNTs were immersed in 0.1 M Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) solution under stirring at room temperature (~25 °C). 0.1 M NaOH solution was added dropwise to the mixture until pH 12.00 was reached. After 24 hours of reaction time, the products were washed with deionized water. After that, the mixed solution was heated with the microwave irradiation using household microwave oven with various irradiation powers 150-450 watts for 5 min. Finally, as-synthesized products were dried for 2 h to obtain the NiO/CNT composites. The structures of the samples were determined by powder X-ray diffraction (X'Pert Pro MPD8 PW3040/60). The morphological images were examined by scanning electron microscopy (JSM-6510). The fine structure of the composite was investigated by transmission electron microscopy (JEOL JEM-2010).

3. Results and Discussion

The XRD patterns of as-prepared NiO/MWCNTs prepared at the irradiation powers of 150-450 watts are illustrated in Fig.1. The peak situated at 25.1° which are observed in all samples is referred to (002) d-spacing of the CNTs (JCPDS-ICDD No.751621) whereas the peaks at 44.8°, 52.1° and 76.4° correspond to the FCC structure of the Ni catalyst used in CNTs synthesis process [17].

For as-synthesized composites, the peaks positioned at $2\theta=35.4°$, 43.7°, and 62.9° attribute to (111), (200), and (220) orientation planes of cubic NiO, respectively (JCPDS-ICDD No.895881). XRD results prove that all composites are mixtures of two phases of NiO and CNT. In addition, it is clearly seen that all specific XRD peaks are prominent, indicating high purity of as-synthesized product and high crystallinity of as-obtained NiO particles. It is noticeable that the peak intensity corresponding to NiO becomes stronger and more intense with increasing of irradiation power suggesting that the formation of NiO nanostructure and crystallinity greatly heighten with increasing irradiation power. The crystalline size of NiO crystallites was calculated from major reflection (111) using the well-known Scherrer's formula:

$$D = K\lambda / (\beta\cos\theta) \quad (1),$$

where D is the crystalline size, K is the shape factor (0.9), λ is the X-ray wavelength (1.5406×10^{-10} m), β is the full-width at half maximum and θ is the Bragg angle. The calculated average crystalline sizes of NiO obtained by this method are approximately 6-8 nm.

Corresponding Author E-mail: pjunlabhut@gmail.com

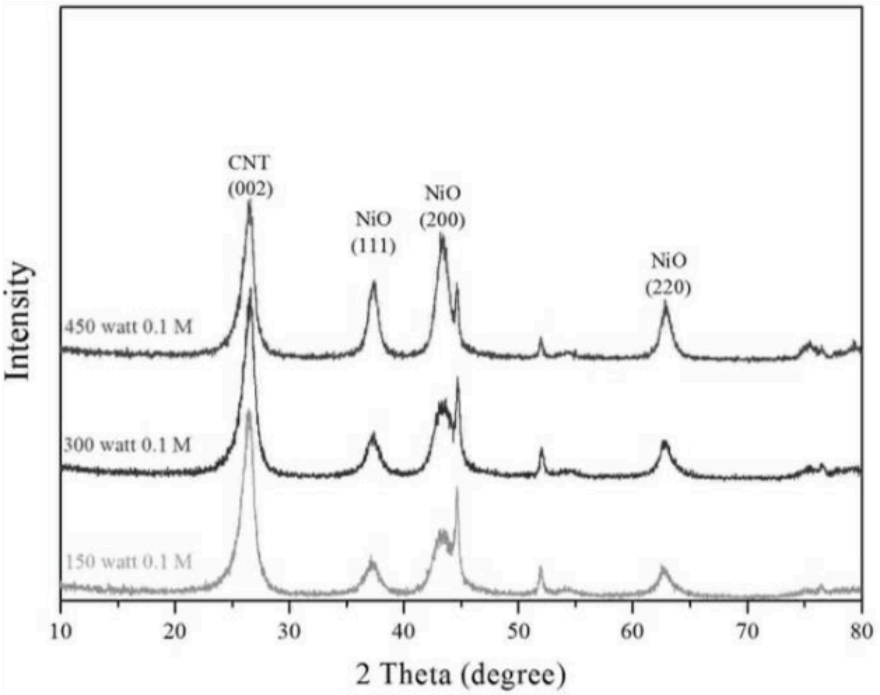

Fig. 1 The XRD patterns of the as-prepared NiO/MWCNTs with various irradiation powers of 150-450 watts.

The morphologies of as-synthesized NiO/MWCNTs were investigated by SEM and TEM. For comparison, Fig. 2 (a) exhibits SEM images of the composites prepared via conventional heating process conducted at 400°C for 2 h. The CNT with diameter of about 50 nm is only observed and its matrix is entangled and cross-linked. The existence of NiO particles onto the CNTs surface was not clearly observed, implying that the impossibility of the formation of NiO onto CNT by conventional heating. SEM images of NiO/MWCNTs synthesized by microwave heating technique with different irradiation power of 150 W and 300 W are illustrated in Fig. 2 (b) and (c), respectively. As observed, the distinguishable results of surface of MWCNTs are obtained. This result indicates that the NiO particles can be synthesized and attached on the surface of MWCNTs by microwave heating technique with low irradiation power and agglomerated to thick wall with the increasing of irradiation power. It is clearly seen that a number of NiO particles are tightly attached to the sidewall of CNTs leading to the well-dispersed network. It is also noticed that the CNT diameter significantly decrease, comparing to pristine CNTs, which may be attributable to the dehydration of CNTs during heating process. Number of NiO nanoparticles adhered to the CNT surface and distribution uniformity seems to increase as irradiation power increases from 150 W to 300 W. The increasing amount of NiO nanoparticles with small sizes can provide greater specific surface area and more active sites for related reactions [18]. This feature could result from the fact that the increasing amounts of heat supplied by microwave irradiation with increasing irradiation power can lead to the better formation of NiO and the binding of NiO particles onto the side wall of CNTs. To ascertain morphology of the obtained sample, NiO/MWNTs composite was further characterized and confirmed by TEM and selected-area electron diffraction (SAED) pattern. As observed in low-magnified TEM

Corresponding Author E-mail: pjunlabhut@gmail.com

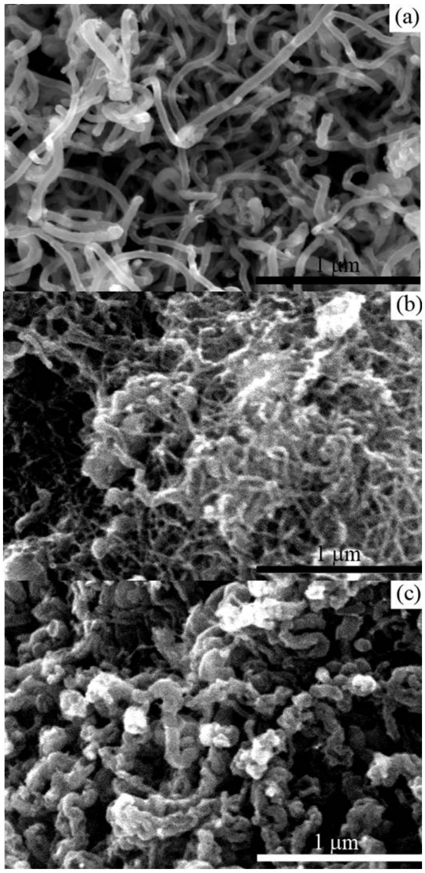

Fig. 2 SEM image of NiO/CNTs heated with conventional heating at 400 ºC for 2 h (a) microwave irradiation heating at 150 watt (b) and 300 watt (c).

images demonstrated in Fig. 3(a) and (b), NiO nanoparticles which are intimately adhered to the CNTs walls are in the combination of nanorod-like structure and quasi-spherical shape structure. The average particle size of NiO is less than 10 nm, which is consistent with the values obtained from the XRD results. HRTEM image exhibited in Fig. 3(c) clearly shows the pattern of the multi-wall of CNTs and the lattice pattern of NiO corresponding to (111) plane of reflection with the d-space of 0.26 nm [19-20]. The inset of Fig. 3(c) shows the corresponding selected area electron diffraction (SAED) pattern of NiO particle. The possible mechanisms involved in the formation of NiO onto CNTs could be described. At first, UV treatment may treat the wall of CNTs with oxygen-containing functional groups [21] which are more reactive than defect-free CNTs. When introduced into treated CNT matrix, Ni^{2+} would likely react on the sidewall of CNTs with the assistance of these defects resulting to intermediate product such as $Ni(OH)_2$ [22]. During uniform heating under microwave irradiation, NiO caused by the dehydration of $Ni(OH)_2$ [23] can be rapidly formed and nucleated on the wall of CNTs by and the composite of NiO and MWCNTs is finally achieved. This reaction may terminate after available defect sites of CNTs are completely covered by NiO particles. All results suggest that the good formation of NiO and CNTs as the composites can be attained with the assistance of microwave heating at intermediate power.

Corresponding Author E-mail: pjunlabhut@gmail.com

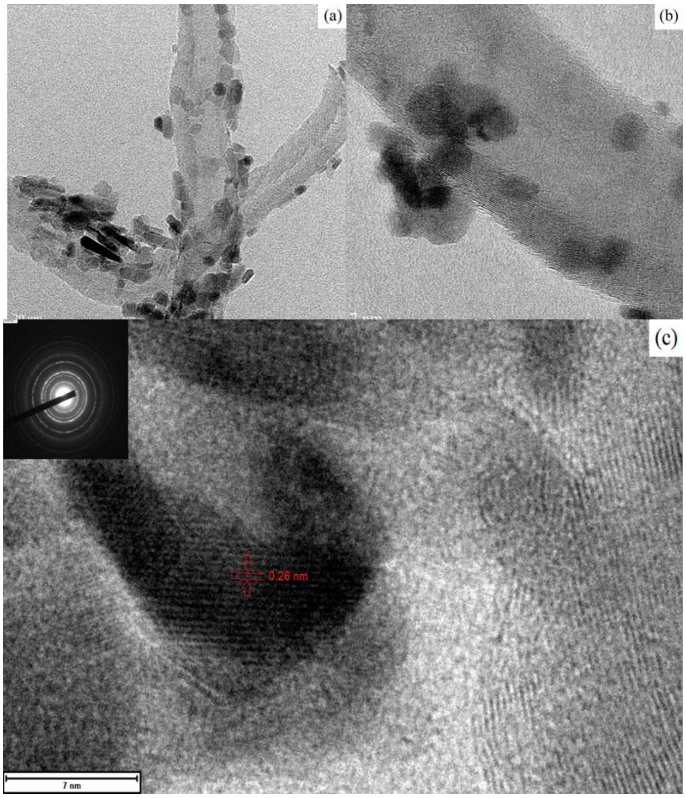

Fig. 3 (a)-(b) Low magnification TEM image of NiO/CNTs and (c) HRTEM image of NiO/CNTs composites and the inset is the corresponding SAED pattern with irradiation power at 150 watt.

4. Conclusions

In summary, NiO/MWCNT nanocomposites were successfully synthesized by a simple and effective microwave-assisted route via a mixture precursor of $NiCl_2 \cdot 6H_2O$ and MWCNTs. The XRD results revealed that the as-prepared nanocomposites contained dual phases of MWCNTs and NiO. SEM and TEM results showed the NiO nanostructures with their size of less than 10 nm are firmly adhered on the surface of CNT and the amount of NiO nanostructures increases with the increase of irradiation power. The formation of NiO onto CNT sidewall may originate from oxygen-containing functional groups initiating the nucleation of NiO and carbon with incorporation of uniform microwave heating at temperate irradiation power.

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Corresponding Author E-mail: pjunlabhut@gmail.com

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Corresponding Author E-mail: pjunlabhut@gmail.com