

Synthesis and characterization of Ni-Si mixed oxide nanocomposite as a catalyst for carbon nanotubes formation

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Ni-Si mixed oxide nanocomposite was prepared by co-precipitation method with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and tetraethylorthosilicate (TEOS) at pH = 10.5 under reflux condition for 6 days. It was then used as a catalyst for the formation of carbon nanotubes (CNTs) by CVD procedure. Characterization of the catalyst and the CNTs was carried out using X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The results showed that Ni-Si mixed oxides nanorods with the average diameter of 3 to 4 nm play a key role in CNTs formation.

Keywords: *Ni-Si mixed oxide, nanocomposite, carbon nanotubes*

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1. Introduction

Carbon nanotubes (CNTs) with extraordinary physical and chemical properties such as small radius curvature at their tips and high chemical and physical stabilities have potential applications in field emission sources [1], hydrogen storage [2], transistors and logic circuits [3, 4] and catalyst supports [5–7]. Since the first discovering, CNTs have been synthesized by three main methods including arc discharge [8–10], laser vaporization [11] and chemical vapor deposition (CVD) [12–14]. Among these, CVD is the unique method which can be executed to achieve vertically aligned growth of CNTs on selected areas of a substrate. There are several techniques in the CVD method such as thermal CVD [15], hot filament CVD [16], Plasma enhanced

(PE) hot-filament CVD [17], microwave PECVD [18]. For commercial applications, the production of CNTs with well defined and organized arrays at a low cost is of fundamental importance. Among the established growth methods, the arc-discharge and laser ablation are challenging with some limitations in the low quantity of CNT products and high temperature requirement which result in prohibitive costs for scale-up mass production of CNTs. These limitations have motivated the development of gas-phase techniques known as catalyst chemical vapor deposition (CCVD), where nanotubes are formed by decomposition of a carbon-containing gas (methane, ethane, acetylene) over a catalyst containing transition metal nanoparticles of Fe, Co and Ni or related oxides, embedded in solid matrices or supported on the surfaces of porous materials. Besides the possibility of mass production at a low cost, this method also has the advantage of control-

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ling the diameter, length and morphology of CNTs by altering the catalyst nanoparticles sizes and deposition conditions [19]. The catalytic supports or matrices which have been employed comprise zeolites [20, 21], mesoporous silica [22], silica [23, 24] and clay minerals [25].

In this study, attempts have been made to prepare Ni-Si mixed oxide nanocomposite and study its application as a catalyst in CCVD system. In contrast to CCVD process which utilizes methane, ethylene, carbon monoxide and ethanol as the common hydrocarbon source [26–30], we have used the inexpensive liquid petroleum gas (LPG) which is a mixture of propane 54 %, butane 45 % and pentane 1 % [31]. On the other hand, by omitting the use of diluted carrier gases (such as hydrogen, argon and ammonia), which are conventionally used in the CCVD synthesis of CNTs, a simpler CVD technique of CNT formation was presented in this article.

2. Experimental

2.1. Preparation of Ni-Si mixed oxide

All materials were obtained from Merck Chemical Company and used without further purification. Ni-Si mixed oxide (NSO) was prepared by the coprecipitation method. $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ (4.3 g in 20 ml water) was slowly added to a solution of tetraethylorthosilicate (TEOS), (16.7 g, 0.8 mol) in water (20 ml). After stirring for 30 min at 50–60 °C, the solution pH was adjusted to 10.5 by addition of aqueous KOH (20 %). The resultant mixture was refluxed at 80 °C for 6 days. The solid product was then filtered and washed with distilled water until the filtrate became neutral. The NiO_2 – SiO_2 solid was dried at 120 °C for 6 h, and then calcined at 800 °C for 6 h. The composition of the catalyst was determined as 20 % NiO_2 and 80 % SiO_2 .

2.2. Preparation of CNTs

The LPG chemical vapor deposition was performed in a quartz tube equipped with temperature and gas-flow controllers, as shown in Fig. 1. The NSO nanocatalyst support was prepared by depositing drops of the ethanol colloidal solution of NSO

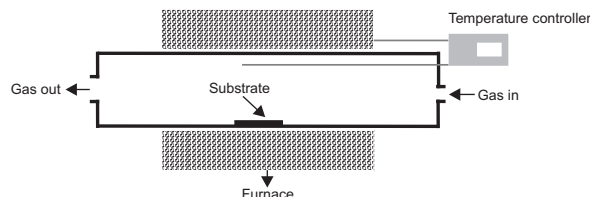


Fig. 1. Schematic diagram of CCVD system.

onto cleaned silicon (111) wafers and letting it to dry up completely at room temperature. After the reactor temperature reached 800 °C the prepared catalyst was placed in the reactor and a flow of LPG (200 sccm) was introduced into the quartz tube. The CNTs growth duration was 20 minutes. The LPG gas was then replaced with nitrogen and the furnace was subsequently cooled to the room temperature.

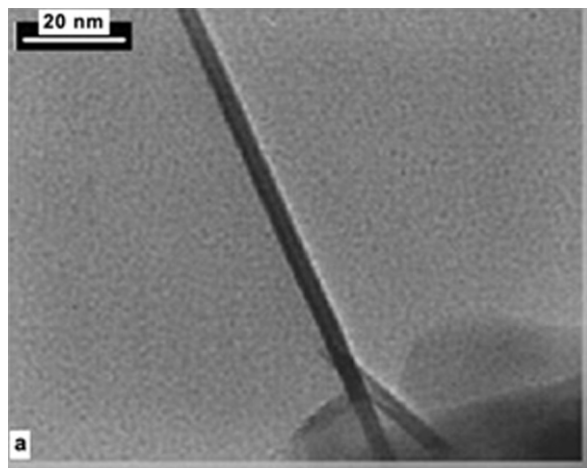
2.3. Characterization

Powder X-ray diffraction (XRD) analysis of the catalyst and CNTs was carried out using a 3003 PTS Seifert diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.1540$ nm). Raman spectra were obtained with Thermo Nicolet Almega Dispersive Micro Raman Spectrometer ($\lambda = 532$ nm). The scanning electron microscopy (SEM) observations were carried out using a Philips XL30 microscope (1992). Transmission electron microscopy (TEM) studies were conducted by a Philips CM-200 FEG (Field Emission Gun) apparatus. X-Ray photoelectron spectroscopy (XPS) was executed in an ESCA/AES system equipped with a concentric hemispherical analyzer (CHA, Specs model EA10 plus). The data acquisition was performed at a nominal resolution of 0.1 eV. For exciting the X-ray photoelectrons, an Al $K\alpha$ line at 1486.6 eV was used.

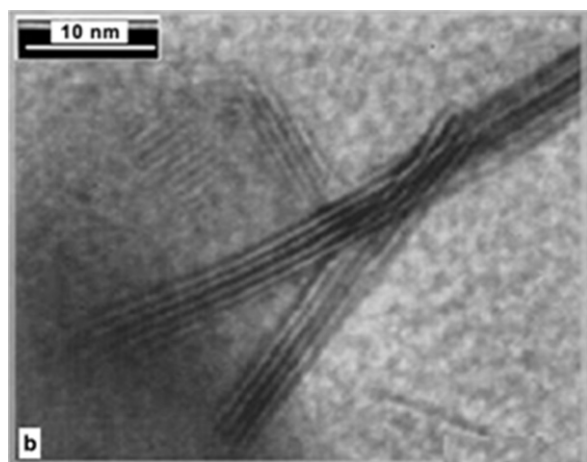
3. Result and discussion

3.1. XRD analysis of NSO nanocomposite

The Ni-Si mixed oxide was prepared as mentioned above with modification of the reaction by using water as a solvent and keeping reaction at reflux condition for six days. The XRD pattern of NSO (calcined at 800 °C), shows NiO_2 as rhombohedral phase (card № 22–1189) on SiO_2 cristobalite



(a)



(b)

Fig. 2. TEM images of Ni-Si mixed oxide nanorods at two different magnifications.

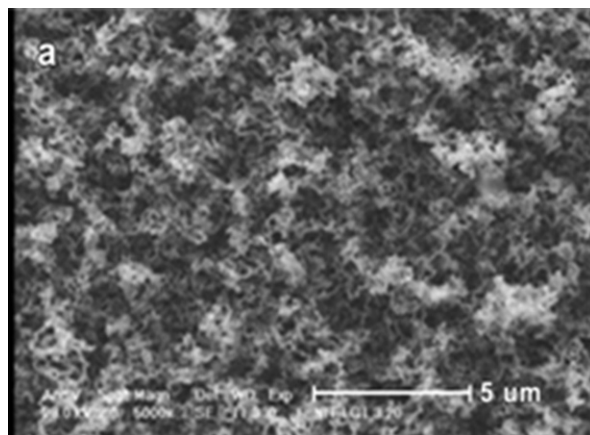
(with card № 39–1425 as tetrahedral phase). The peaks were relatively broad with low intensities that implied fine particles.

3.2. TEM images of NSO

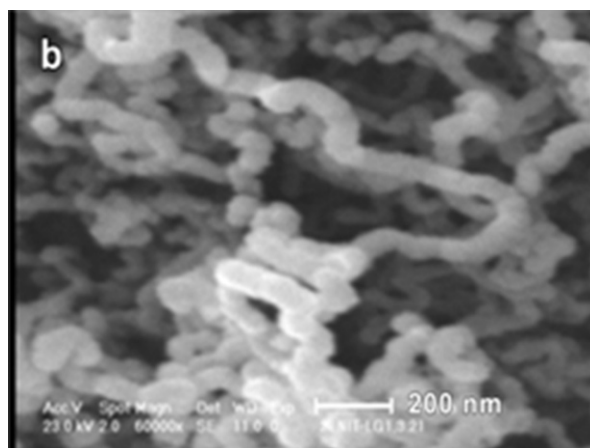
Fig. 2a and 2b display the TEM images of Ni-Si mixed oxide at two different magnifications. The formation of nanorods with 5 sheets and with the same interspace and diameter of 3–4 nm is interesting for further studies.

3.3. SEM and TEM images of CNTs

Fig. 3a and 3b show SEM images of the obtained CNTs at low and high magnifications, respectively.



(a)



(b)

Fig. 3. SEM images of the grown CNTs at two different magnifications.

Based on these Figures, a dense forest of CNTs has grown on the wafer. The histogram of the grown CNTs, fitted with a Gaussian curve is illustrated in Fig. 4. According to this diagram the average diameter of the grown CNTs is 37 nm. Fig. 3 also shows that the length of obtained CNTs reaches to several microns.

Fig. 5 exhibits the TEM images of the grown CNTs. This figure shows that the morphologies seen in the SEM images have tubular structures, i.e. they are carbon nanotubes and not carbon fibers. The dark point indicated by the black arrow in Fig. 5a shows the catalyst particle on the tip of the tube. The white arrows in Fig. 5b show the graphitic shells

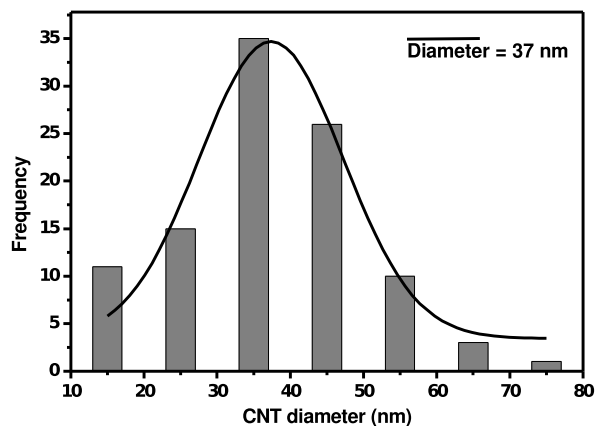


Fig. 4. Histogram of diameter distribution of the grown CNTs.

that block the interior of the tubes, characteristic of bamboo shaped structure.

3.4. XPS Spectrum of CNTs

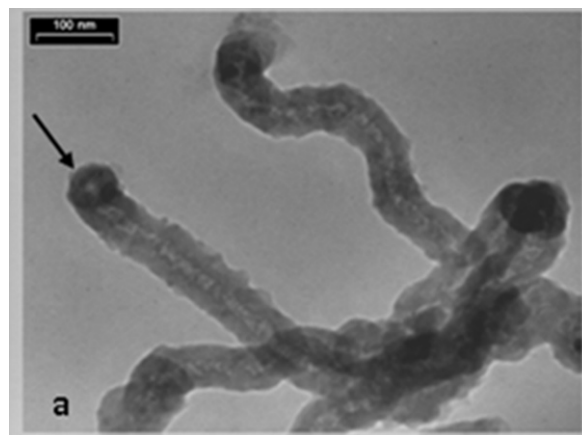
Fig. 6 demonstrates a deconvolution of carbon 1s peak in a XPS spectrum of the grown CNTs. As it can be seen, there are four peaks. These peaks are attributed to SP^2 , SP^3 , C–O and C–OH chemical bonds at 284.4 eV, 285.1 eV, 286.77 eV and 289.82 eV, respectively.

According to this spectrum, graphite is the major part of the carbon structure in the samples, which is another evidence of the growth of CNTs in our process.

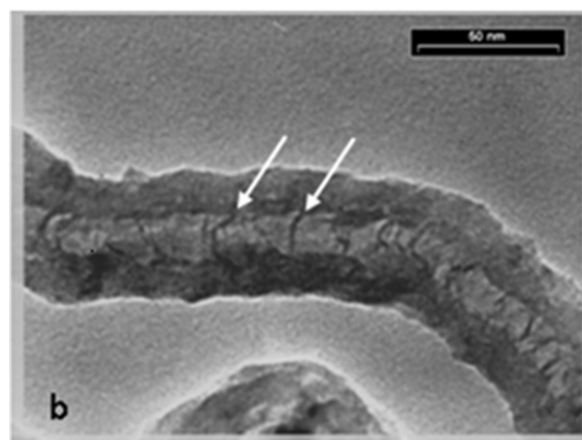
3.5. Raman Study

Raman spectroscopy was used to further characterize the structure and crystallinity of the synthesized CNTs. The Raman spectrum of the produced CNTs is depicted in Fig. 7. The Raman band appearing in $1500\text{--}1605\text{ cm}^{-1}$ region of the wave number is attributed to G band (graphite band) and the one appearing in $1250\text{--}1450\text{ cm}^{-1}$ spectral region is known as D band (disorder induced band). The G band is assigned to C–C vibration frequency of the carbon material with a sp^2 orbital structure and the D band is contributed to the disorder induced vibration of C–C band [32]. Here there are two main peaks in the spectrum.

The clear G-band at 1588.7 cm^{-1} indicates the formation of graphitized multi wall carbon nano-



(a)



(b)

Fig. 5. TEM images of the grown CNTs.

tubes (MWCNTs) and the D-band at 1317.8 cm^{-1} indicates the existence of the disordered carbon such as amorphous carbonaceous particles or defective graphite layers. The peak intensity ratio $I(G)/I(D)$ is used as a rough measure of sample quality because it is the relative response of graphite carbon to defective carbon. Here the ratio of $I(G)/I(D)$ is ~ 1.10 which shows that the grown CNTs have acceptable crystalline graphitic structure.

Based on the obtained results, it is observed that NSO nanorods have been formed in the presented conditions. Nowadays, the study of mixed oxide nanorods formation is an interesting subject. It is generally accepted that the CNT growth processes involve the adsorption and decomposition of LPG containing carbon on a catalyst surface, the disso-

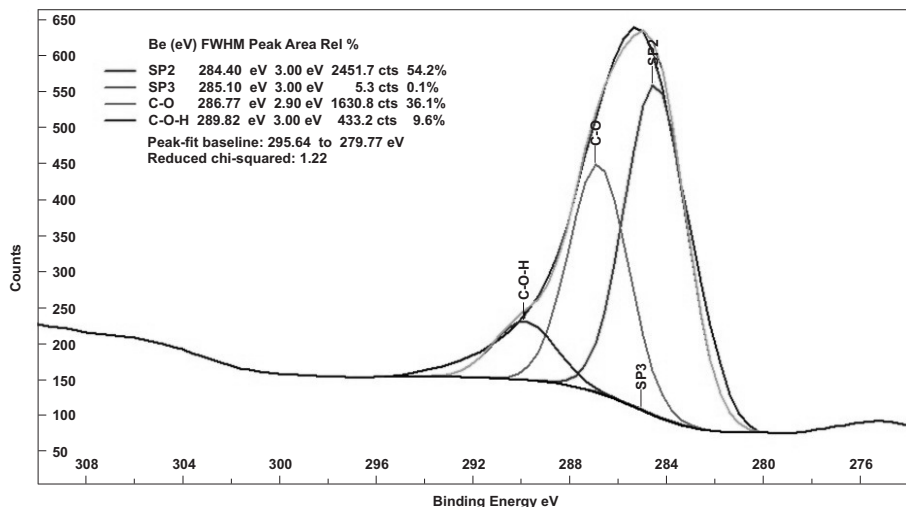


Fig. 6. XPS spectroscopy of CNTs.

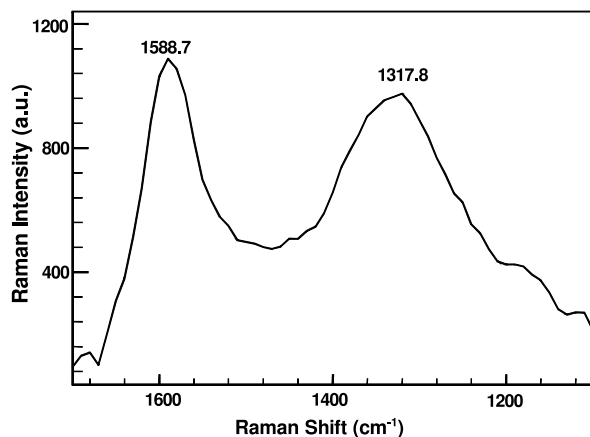


Fig. 7. Raman spectrum of CNTs.

lution and diffusion of released carbon atoms dissolved in the catalyst particles and the precipitation of the graphite-like layers [16].

4. Conclusion

In this study, a nanocomposite of Ni-Si mixed oxide was synthesized by co-precipitation method in water as a green solvent without using any organic template. Attempts have also been made to prepare these nanostructures with only one morphology. The SEM-EDX, and TEM-EDX showed that these nanomaterials were mainly Ni and Si oxides with the molar ratio of one to four. The prepared nanocomposite shows a good activity as a catalyst for mass

production of CNTs with LPG which is a relatively cheap carbon source. The growth mechanism was investigated by examining the SEM, TEM, Raman and XPS. The TEM image implies the formation of Ni-Si mixed oxide nanocomposite as nanorods. Without using any catalyst, and at 550–650 °C, no LPG decomposition was observed. It was also found that, with no nickel oxide present in the mixed oxides, no CNTs were formed. The CCVD process with the eco-friendly synthesis Ni-Si mixed oxide is a suitable procedure for the mass production of CNTs.

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References

- [1] DE-HEERW A., CHATELAIN A., UGARTE D.A., *Science*, 270 (1995), 1179.
- [2] CHENG H.M., YANG Q.H., LIU C., *Carbon*, 39 (2001), 1447.
- [3] DERYCKE V., MARTEL R., APPENZELLER J., AVOURIS PH., *Nano Lett.*, .
- [4] TANS S.J., VERSCHUREN R.M., DEKKER C., *Nature*, 1 (2001), 453.
- [5] PLANEIX J.M., COUSTEL N., COQ B., BROTONS V., *J. Am. Chem. Soc.*, 116 (1994), 7935.
- [6] LUO J.Z., GAO L.Z., LEUNG Y.L., AU C.T., *Catal. Lett.*, 66 (2000), 91.
- [7] DONG X., ZHANG H.B., LIN G.D., YUAN Y.Z., *Catal. Lett.*, 85 (2003), 237.

- [8] IJIMA S., *Nature*, 354 (1991), 56.
- [9] IJIMA S., ICHIHASHI T., *Nature*, 363 (1993) 603.
- [10] SATIO Y., TANI Y., MIYAGAWA N., MITSUSHIMA K., *Chem. Phys. Lett.*, 294 (1998), 593.
- [11] YUDASAKA M., KOMATSU T., ICHIHASHI T., IJIMA S., *Chem. Phys. Lett.*, 278 (1997), 102.
- [12] BIRKEETT P.R., CHEETMAN A.J., EGGEN B.R., HARE J.P., *Chem. Phys. Lett.*, 281 (1997), 111.
- [13] XU X.-J., HUANG S.-M., *Mater. Lett.*, 61 (2007), 4235.
- [14] KUNADIAN I., ANDREWS R., QIAN D., PINAR MENGUC M., *Carbon*, 47 (2009), 384.
- [15] IHM K., KANG T.-H., LEE D. H., PARK S.-Y., KIM K.-J., KIM B., YANG J.-H., PARK C.-Y., *Surf. Sci.*, 600 (2006), 3729.
- [16] REN Z.F., HUANY Z.P., XU J.W., WANG J.H., BUSH P., SIEGAL M. PROVENICO P.N., *Science*, 282 (1998), 1105.
- [17] CHOI Y.C., SHIN Y.M., LEE Y.H., LEE B.S., PARK G.S., CHOI W.B., LEEN S., KIM J.M., *Appl. Phys. Lett.*, 76 (2000), 2367.
- [18] CHHOWALLA M., TEO K., AMARATUNGA G.A.J., FERRARI A.C., ROY D., ROBERTSON J., MILNE W. I., *J. Appl. Phys.*, 90 (2001), 530.
- [19] TRIANTAFYLHIDIS K.S., KARAKOULIA S.A., GOURNIS D., DELIMITS A., NALBANDIAN L., MACCALLINI E., RUDOLF R., *Micropor. Mesopor. Mater.*, 110 (2008), 128.
- [20] FONSECA A., HERNADI K., NAGY J.B., BERNAERTS D., LUCAS A., *J. Mol. Catal. A*, 107 (1996), 159.
- [21] MARTIN I., RIUS G., ATIENZAR P., TERUEL L., MESTERS N., PEREZ-MURANO F., GARCIA H., GODIGNON P., CORMA A., LORA-TAMAYO E., *Microelectronic Engineering*, 8 (2008), 1202.
- [22] LIM S., CIUPARU D., PAK C., DOBEK F., CHEN Y., HARDINGA D., PFEFFERLE L., HALLER G., *J. Phys. Chem. B*, 107 (2003), 11048.
- [23] HERNADIA K., FONSECA A., NAGY J.B., BERNEAERTS D., LUCAS A.A., *Carbon*, 34 (1996), 1249.
- [24] LI J., LU G., *Appl. Catal. A: Gen.*, 273 (2004), 163.
- [25] GOURNIS D., KARAKASSIDES M.A., BAKES T., BUKOS N., PETRIDIS D., *Carbon*, 40 (2002), 2641.
- [26] CASSEL A.M., RAYMAKERS J.A., KONG J., DAI H., *J. Phys. Chem.B*, 103 (1999), 6484.
- [27] HAFNER J., BRONIKOWSKI M., AZAMIAN B., NIKOLAEV P., COLBERT P., SMALLEY R., *Chem. Phys. Lett.*, 296 (1998), 195.
- [28] PAN Z.W., XIE S.S., CHANG B.H., WANG C.Y., LU L., LIU W., ZHOU W.Y., LI W.Z. , QIANL X., *Nature*, 394 (1998), 631.
- [29] LYU S.C., LIU B.C., LEE T.J., YANG C.W., PARK C.Y., LEE C., *J. Chem. Commun.*, (2003), 734.
- [30] FLAHAUT E., BACSA R., PEIGNEY A., LAURENT C., *Chem. Commun.*, (2003), 1442.
- [31] AKBARZADEH PASH A.M., SHFIEKHANI A., VESAGHI M.A., *Appl. Surf. Sci.*, 256 (2009) 1365.
- [32] DRESSSELHAUS M.S., DRESSSELHAUS G., JORIO A., SOUZA FILHO A.G., SAITO R., *Carbon*, 40 (2002) 2045.

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