Solvothermal Synthesis of Copper Nanoparticles Loaded on Multi-wall Carbon Nanotubes as Catalyst for Thermal Decomposition of Ammonium Perchlorate

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ABSTRACT

Copper nanoparticles were synthesized on multiwall carbon nanotubes, (Cu)/(MWCNTs), based on the solvothermal method. The used reagents include MWCNTs, cupric nitrate trihydrate (Cu (NO3)2.3H2O), diethylene glycol (DEG), and diethanol amine. Characterization of Cu/MWCNTS nanoparticles was performed by Fourier transform infrared spectroscopy (FTIR), Ramanspectroscopy, X-ray diffraction spectroscopy (XRD), Inductively coupled plasma (ICP), differential scanning calorimeter (DSC), and Field Emission Scanning Electron Microscopy (FE-SEM).The results showed that the surface of MWCNTs is covered by Cu nanoparticles, and the diameter of Cu/MWCNTs nanoparticles gets larger than that of MWCNTs. Furthermore, in the presence of the Cu/MWCNTs composite particles, the synthesized Cu/MWCNTs showed 95% Cu loaded on the MWCNTs.The results showed that using 3 wt.% Cu/MWCNTs nanocatalyst lowered the decomposition temperature of AP by 121.76 °C. The totalenthalpy for this case was 1384.46 J g -1. This work indicates that the catalytic performance of Cu/MWCNTs can improvethe thermal decomposition of AP.

1. Introduction

Ammonium perchlorate is one of the most oxidizing materials in missile solid propellant and has interesting effects on the missile solid propellant [1]. The burning rate of propellant is an important parameter on combustion properties of ammonium perchlorate[2]. The lower the decomposition temperature of the material, the better the combustion properties will be [3, 4]. One of the other parameters is the enthalpy of combustion. The higher the enthalpy, the better the combustion properties will be [5, 6].One way of improving these parameters is to use one or more catalysts besides ammonium perchlorate. It is obvious that the nano-sized catalysts are more suitable than other typical catalysts [7, 8].

Today, the effects of different catalysts on thermal decomposition of ammonium perchlorate in solid propellant were reported by many researches. For example, nano particles are very good candidates due to their very small particle size and high surface area. Researchers have come to the conclusion that

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catalysts and specially nano catalysts accelerate the burning rate of the propellant by lowering ammonium perchlorate thermal decomposition temperature [9-12].

There are several methods for synthesis of nano-sized catalysts and its deposition on the surface of carbon nanotubes. Among them, solvothermal process consists of the heterogeneous chemical reactions in the presence of solvents (aqueous or non-aqueous) in an ambient temperature and atmospheric pressure in a closed system. The main advantages of the solvothermal method are low temperature, short reaction time, low cost, control of particle size, homogeneity, preventing the degradation of some compounds in high temperatures, preventing the vapor pressure of the material, allowing the mass production of crystals with uniformity and desirable quality to avoid the formation of non-homogeneous compound, the ability to control atmospheric conditions, and reducing the possibility of synthesizing oxide materials under certain solvothermal process [6].

Many reports show the use of catalysts or nano-catalysts in this topic. Yang et al. [13] lowered decomposition temperature of ammonium perchlorate by using MgO as catalyst. Zhang et al. [14] studied Fe_2O_3 as catalyst and showed a decrease in decomposition temperature of ammonium perchlorate from 436.4°C to 387.5°C.In another study, Linsheng et al. [15] utilized $CuFe_2O_4$ for thesame purpose and reported a decrease in temperature from 445 to 351°C. Using Cu_2O as physical admixture by ammonium perchlorate showed a decrease in decomposition temperature from 439 to 348°C [16]. In another study, physical admixture of $CuCr_2O_4$with ammonium perchlorate caused a decrease in decomposition temperature of ammonium perchlorate from 467 to 349°C [6]. Li et al. [17] used Ni/CNTs catalyst and experienced temperature decrease of ammonium perchlorate decomposition from 446.5 to 346°C. Ping et al. [18] used Cu, a compound of Cu and CNT, and Cu/CNT followed by physical mixing with ammonium perchlorate and reported a decrease in decomposition temperature of this material from 478.1 to 395.4, 363.2, and 351.8°C, respectively. In most works, using pure carbon nano-tubes is an essential [19]. The use of carbon nano-tubes as substrate for catalysts improves catalytic activity because of their unique properties like small size and high surface area [20].

Although there are several studies in literature in this field, using Cu/MWCNTs synthesis via methods such as solvothermal in which Cu/MWCNT is used as catalyst in thermal decomposition of ammonium perchlorate is not addressed yet. Thus, in this research, in addition to present an approach to Cu/MWCNTs synthesis, this material is used as catalyst in thermal decomposition of ammonium perchlorate. In so doing, the effects of temperature decrease and enthalpy increase in decomposition of ammonium perchlorate are discussed.

2. Experimental

2. 1. Materials and methods

The used reagents include MWCNTs (National Iranian Oil Company), cupric nitrate trihydrate (Cu $(NO_3)_2.3H_2O$), diethylene glycol (DEG), and diethanol amine (DEA, India Co LOBA Chemie). The analytical instruments used in this research are FE-SEM (Hitachi S416002, Holland), DSC (Mettler Toledo Gmbh, Switzerland), XRD (Model: Xpert-MPD, Cu: Philips, Holland, λ: 1.54056), ICP (Model: VISTA-PRO, Co: varian, Australia).

The Cu/MWCNTs were prepared by solvothermal method. Cu $(NO_3)_2.3H_2O$ (0.75 mmol) was dissolved in 10 ml of DEG at 95 °C in an oil bath. After 30 min of stirring, 3 ml of DEA was injected into the above hot solution. Then, NaOH (6 mmol) was dissolved in 5 ml of hot DEG and was introduced into the mixture. After another 15 min of stirring, 20 mg of purified MWCNTs was fully dispersed in 12 ml of DEG, followed by 30 min of vigorous stirring. The mixture was then transferred to a Teflon-lined autoclave of 50 ml capacity, and the sealed autoclave was maintained at 190 °C for 8 h. Finally, the composite was isolated by centrifugation, rinsed repeatedly with deionized water, and then dried under vacuum.

3. Results and discussion

3. 1. Infrared Spectroscopy Analysis

Fig. 1 shows the FT-IR patterns of the

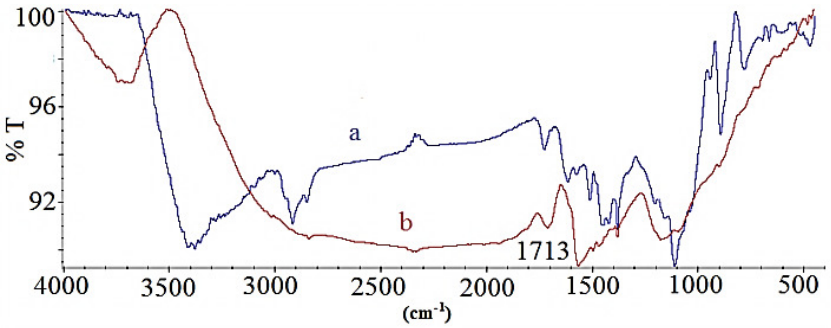

Fig. 1. FT-IR patterns of carbon nanotubes: (a) unmodified carbon nanotubes; (b) carbon nanotubes purified by acid.

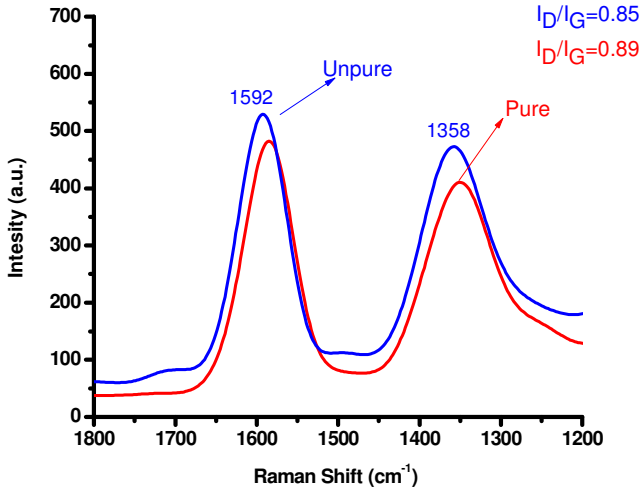

Fig. 2. Raman spectra of Unpure-MWCNTs and acid-treated MWCNTs.

unmodified and modified MWCNTs. From the FT-IR patterns, a carboxyl group peak at 1713 $cm^{-1}$and a hydroxyl group peak at 3384 cm^{-1}can be seen, respectively. It shows that the functionalizing process has performed perfectly.

3. 2. Raman Analysis

Figure 2 shows the Raman spectra of impure MWCNTs and acid-treated MWCNTs. The D band is attributed to defects in the disorder induced modes (or sp^3-hybridized carbons) and the G band is related to graphitic wall inner planes vibrations (or sp^2-hybridized carbons). The D band at 1358 cm^{-1} and G band at 1592 cm^{-1} characterized by Raman spectroscopy, showed the I_D/I_G area 0.85 and 0.89, respectively.

3. 3. XRDAnalysis

The crystalline structure of catalyst was characterized by XRD. As shown in Fig. 3, copper and graphite reflectionplanes coincide to the Standard (JCPDS no. 00-003-1005), and (JCPDSno. 12-0212), respectively. The copper and graphitic crystal structures confirmed to copper and carbon nanotubes, respectively.In the pattern assigned to copper, diffraction peaks at around 43.39, 50.47, 74.80, 89.86, 95.12 and 26.14° correspond to the (111), (200), (220), (311), and (222) reflections, respectively. Diffraction peak at 26.41° can be indexed to the (002) reflection of the MWCNTs. The large peak widths are ascribed to the formation of nano sized particles of Cu. The size of particles were calculated by Scherrer equation [21, 22] using the (111) peak (2θ = 43.39) which is 41 nm.

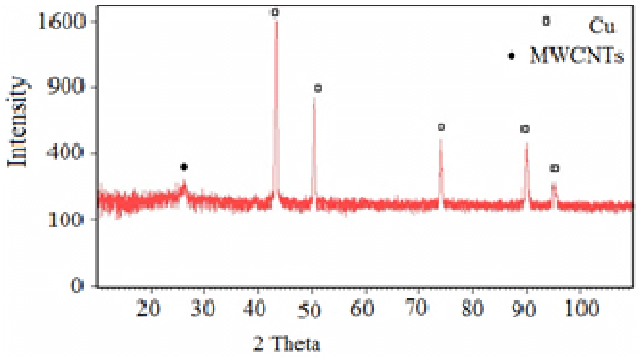

Fig. 3. XRD pattern of Cu/MWCNTs

Table 1. Results from the testing of copper by the ICP analysis

Sample	EI	Wavelength (nm).	Units	Conc.	Int.(c/s)
Water	Cu	324.754	$\mu g\ mL^{-1}$	0.0	10.515
Cu-20	Cu	324.754	$\mu g\ mL^{-1}$	20	57506
Cu-50	Cu	324.754	$\mu g\ mL^{-1}$	50	142605
Cu-100	Cu	324.754	$\mu g\ mL^{-1}$	100	282014
Cu-Sample	Cu	324.754	$\mu g\ mL^{-1}$	X	7073.5

3. 4. ICPAnalysis

The copper content in the remained solution was measured by ICP instrument to obtain the copper content in the Cu/MWCNTs catalyst. The initial value of copper was 47.34 mg. Inductive coupled plasma (ICP) experiments have shown that 45.11 mg copper was deposited on multiwall carbon nanotubes, which is approximately 95% of total content. The results are summarized in Table 1.

3. 5. FE-SEM Characterization

The surface morphologies of the prepared MWCNTs and Cu/MWCNTs were investigated by FE-SEM and the micrographs have been outlined in Fig. 4. As can be seen, the MWCNTs have very smooth surfaces. A comparison of Fig. 4a and 4b reveals that the surface of MWCNTs isnot smooth. The results of FE-SEM showed that Cu nanoparticles are loaded on the surface of MWCNTs.

3. 6. Thermal Analysis

Fig .5 shows the DSC curve for pure AP and for physical mixture of AP and 3 wt.-% Cu/MWCNTs at 10 $^{o}C\ min^{-1}$. The endothermic DSC peak at 247.44 ^{o}C in pure AP is due to the crystallographic transition from orthorhombic to cubic form. This transition remains unaltered (or partially altered) after the addition of Cu/MWCNTs. In pure AP, the first low temperature exothermic peak (LTD) at 309.52 ^{o}C is attributed to the partial decomposition of AP, while the second and main high temperature exothermic (HTD) at 437.39 ^{o}C corresponds to complete decomposition of the intermediate products into volatile products.

After the addition of Cu/MWCNTs, noticeable changes were observed in high temperature decomposition (HTD) of AP. Figure 5 shows the decomposition of AP in the presence of MWCNTs at the heating rate of10 $^{o}C\ min^{-1}$. The position of the exothermic strongly depends on the size of the functionalized MWCNTs. Compared to pure AP, the HTD has been observed to shift from 437.39 (pure AP) to 315.53 ^{o}C (AP and 3wt.% Cu/MWCNTs), at 10 $^{o}C\ min^{-1}$. This drastic decrease in temperature by 121.76 ^{o}C indicates an efficient catalytic effect on the thermal decomposition of AP. The decrease is more significant in Cu/MWCNTs due to the

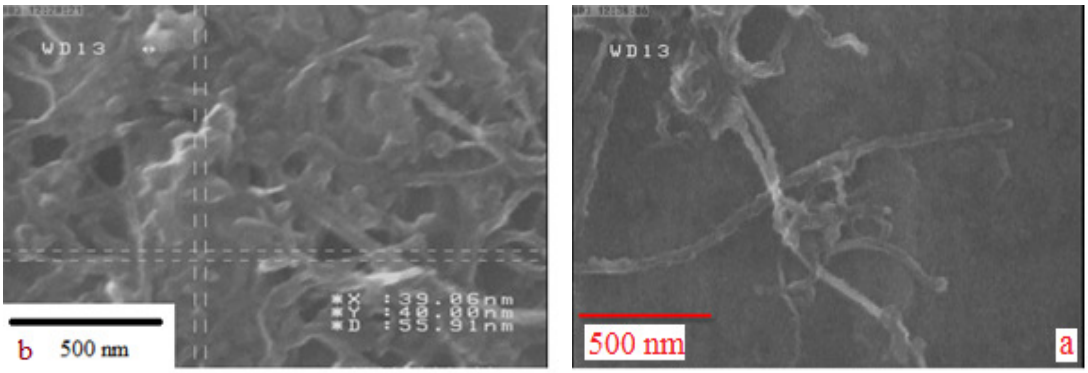

Fig. 4: SEM micrographs of (a) raw MWCNTs; (b) Cu/MWCNTs

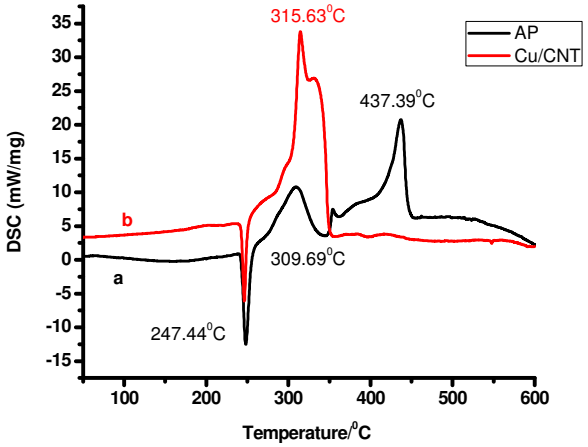

Fig. 5. DSC patterns of different samples: (a) pure AP and (b) mixture samples of Cu/MWCNTs and AP

synergistic action of the binary (AP and 3 wt.% Cu/MWCNTs) causing an enhancement in the catalytic activity. Such a marked reduction in HTD is also attributed to the presence of a large number of active sites, higher surface area, and smaller size of Cu/MWCNTs. Another interesting observation was a high heat release (ΔH) of 1384.46Jg^{-1} (3 wt.-% Cu/MWCNTs) compared to 388.86 Jg^{-1} for pure AP, which is the highest value achieved so far by using Cu/MWCNTs catalyst.

4. Mechanism of thermal decomposition of AP

For the thermal decomposition of ammonium perchlorate, two major mechanisms have been proposed. First: electron transfer from perchlorate ion to ammonium ion, which is as follows:

$$ClO_4^- + NH_4^+ \rightarrow ClO_4^\circ + NH_4^\circ \quad [1]$$

Second: proton transfer from ammonium ion to perchlorate ion, which is as follows:

$$NH_4ClO_{4(S)} \rightarrow NH_4^+ + ClO_4^- \rightarrow NH_{3(S)} + HClO_{4(S)} \rightarrow NH_{3(g)} + HClO_{4(g)} \quad [2]$$

In this study, the Cu/MWCNTs provide a bridge for the transfer of electrons from the perchlorate ions to the ammonium ions. The mechanism can be explained by the notion that the presence of a partially filled-3d orbital of Cu^{2+}. Cu^{2+} ($3d^9$) can easily accept the released electron from ClO_4^- to form stable full-filled 3d-orbital Cu^+ ($3d^{10}$) cation, as follows:

$$NH_4ClO_4 \rightarrow NH_4^+ + ClO_4^- \quad [3]$$

$$Cu^{+2} + ClO_4^- \rightarrow Cu^+ + ClO_4 \quad [4]$$

$$Cu^{+} + NH_4^{+} \rightarrow Cu^{+2} + NH_4 \quad [5]$$

The catalytic effect of Cu/MWCNTs is observed to be significant on the HTD process and considerably less on LTD. This is because Cu/MWCNTs probably create positive holes and electrons due to the existence of lattice defects in Cu^{2+}. These positive holes and active sites in Cu/MWCNTs are associated with the adsorption of electron exchange and gaseous products. In addition, MWCNTs nanoparticles are good catalysts by themselves and that is why the catalytic properties of Cu/MWCNTs were improved. Therefore, this exhibits HTD at lower temperature with increase in catalytic efficiency.

5. Conclusions

The following results were obtained.

1- The solvothermal method revealed to be a successful route for the preparation of nanocrystalline Cu/MWCNTs.

2- The crystallite size of nanoparticles was determined to be 41 nm.

3- The purification and functionalization of raw MWCNTs were achieved by concentration of 7.0 mole / L nitric acid.

4- Carboxylation and hydroxyl group peaks for carbon nanotubes in the final product, characterized by FT-IR, were observed at 1713 cm^{-1} and 3384 cm^{-1}, respectively.

5- The D band at 1358 cm^{-1} and the G band at 1592 cm^{-1}characterized by Raman spectroscopy, showed the I_D/I_G area 0.85 and 0.89, respectively.

6- The diffraction peak of MWCNTs at $2\theta=26.14°$ can be attributed to the (002)plane and copper, while diffraction peaks at around 43.39, 50.47, 74.80, 89.86, 95.12 correspond to the (111), (200), (220), (311), (222) reflections, respectively.

7- Diffraction peak at 26.41° can be indexed to the (002) reflection of the MWCNTs.

8- The peak of the high-temperature decomposition of AP declined about 121.76°C.

9- High released heat (ΔH) is 1384.46 J $g^{-1}$for mixed samples (AP 3 wt.-% Cu/MWCNTs) and is 388.86 J g^{-1} for pure AP.

References

1. Z. Yu, L. Chen, L. Lu and X. Yung, DSC/TG-MS Study on in Situ Catalytic Thermal Decomposition of Ammonium Perchlorate over CoC2O4,Chin. J. Cata., Vol. 30, 2009, pp. 19–23.
2. L. J. Chen, G. S. Li, P. Qi andL.P. Li, Thermal Decomposition of Ammonium Perchlorate Activated Via Addition of NiONanocrystals,J. Therm. Anal. Calorm, Vol. 92, 2008, pp.765–769.
3. Z. Yu, Y. Sun, W. Wei, L. Lu andX. Wang, Preparation of NdCrO3 Nanoparticles and their Catalytic activity in the Thermal Decomposition of Ammonium Perchlorate by DSC/TG-MS,J. Therm. Anal. Calorm,Vol. 97, 2009, pp. 903–909.
4. X. Han, Y. L. Sun, T. F. Wang, Z. K. Lin, S. F. Li, F. Q. Zhao, Z. R. Liu, J. H. Yi and X. N. Ren, Thermal Decomposition of Ammonium Perchlorate Based Mixture With Fullerenes.J. Therm. Anal. Calorm, Vol. 91, 2008, pp. 551–557.
5. P. R. Patil, V. N. Krishnamurthy andS. S. Joshi, Joshi SS. Differential Scaning Calorimetry Study of HTPB based Composite Propellants in Presence of Nano Ferric OxidePropellants, Explos. Pyrotech, Vol. 31, 2006, pp. 442-446.
6. P. R. Patil, V. N. Krishnamurthy and S. S. Joshi, Effect of Nano-Copper Oxide and Copper Chromite on the Thermal Decomposition of Ammonium Perchlorate, Propellants, Explos. Pyrotech, Vol. 33, 2008, pp. 266-270.
7. L. Chen, L. Li andG. Li, J. Synthesis of CuONanorods and their Catalytic activity in the Thermal Decomposition of Ammonium Perchlorate,Alloys Compd, Vol. 464, 2008, pp. 532–536.
8. L. L. Liu, F. S. Li, L. H. Tan, L. Ming andY. Yi, Effect of Nano-Copper Oxide and Copper Chromite on the Thermal Decomposition of Ammonium Perchlorate,Propellants, Explos. Pyrotech,Vol. 29, 2004, pp. 34-38.
9. S. S. Joshi, P. R. Patil and V. N. Krishnamurthy, Thermal Decomposition of Ammonium Perchlorate in the Presence of Nanosized Ferric Oxide, Defence. Sci. J, Vol. 58, 2008, pp. 721-727.
10. X. Hua, W. Xiaobing andZ. Li, Selective Preparation of Nanorods and Micro-Octahedrons of Fe2O3 and their Catalytic Performances for Thermal Decomposition of Ammonium Perchlorate, Powder Technol, Vol. 185, 2008, pp. 176–180.
11. Z. Ma, F. Li andH. Bai, Effect of Fe2O3 in Fe2O3/AP Composite Particles on Thermal Decomposition of AP and on Burning Rate of the Composite Propellant, Propellants, Explos. Pyrotech, Vol. 91, 2006, pp. 447-451.

12. Z. Ma, F. Li andA. Chen, Preparation and Thermal Decomposition Behavior of TMOs/AP Composite Nanoparticles, J NanoSci, Vol. 11, 2006, pp. 142-145.
13. G. Duan, X. Yang, J. Chen, G. Huang, L. Lu and X. Wang, The Catalytic Effect of nanosizedMgO on the Decomposition of Ammonium Perchlorate, Powder Technol, Vol. 172, 2007, pp. 27–29.
14. Y. Zhang, X. Liu, J. Nie, L. Yu andY. Zhong, Improve the Catalytic activity of a-Fe2O3 Particles in Decomposition of Ammonium Perchlorate by Coating Amorphous Carbon on their Surface, J. Solid State Chem, Vol. 184, 2011, pp. 387-890.
15. T. Liu, L. Wang, P. Yang andB. Hu, Preparation of Nanometer CuFe2O4 by auto-Combustion and its Catalytic activity on the Thermal Decomposition of Ammonium Perchlorate, Mater. Lett, Vol. 62, 2008, pp. 4056–4058.
16. B. Henga, T. Xiao, X. Hu, M. Yuan, W. Tao, W. Huang andY. Tang, Catalytic activity of Cu2O Micro-Particles with Different Morphologies in the Thermal Decomposition of Ammonium Perchlorate, Thermochim. Acta, Vol. 524, 2011, pp. 135-139.
17. X. J. Zhang, W. Jiang, D. Song, J. X. Liu and F. S. Li, Preparation and Catalytic activity of Ni/CNTs Nanocomposites using Microwave Irradiation Heating, Mater. Lett, Vol. 26, 2008, pp. 2343–2346.
18. C. Ping, F. Li, Z. Jian andJ. Wei, Preparation of Cu/CNT Composite Particles and Catalytic Performance on Thermal Decomposition of Ammonium Perchlorate, Propellants, Explos. Pyrotec, Vol. 31, 2006, pp. 452-455.
19. W. Jiang, Y. Liu, F. Li, J. Chu andK. Chen, Superparamagnetic Cobalt-Ferrite-Modified Carbon Nanotubes Using a Facile Method, Mater. Sci. Eng, Vol. 166, 2010,pp. 132-134.
20. D. N. Bui, S. Z. Kang, L. Qin,X.Q. Li and J. Mu, Relationship between the Electrochemical Behavior of Multiwalled Carbon Nanotubes (MWNTs) Loaded with CuO and the Photocatalytic activity of Eosin Y-MWNTs-CuO System, Appl. Surf. Sci, Vol. 258, 2012, pp. 2836-2843.
21. N. A. Smith, N. Sekido, J. H. Perepezko, A. B. Ellis and W. C. Crone, Ellis AB, Crone WC. Synthesis of Dual Phase Bronze Alloys from Elemental Nanoparticle Constituents, J. Scr. Mater, Vol. 51, 2004, pp. 423–426.
22. D. Saberi, M. Sheykhan, K. Niknamand A. Heydari, Preparation of Carbon Nanotube-Supported a-Fe2O3@CuO Nanocomposite: a Highly Efficient and Magnetically Separable Catalyst in Cross-Coupling of Aryl Halides with Phenols, J. Catal. Sci. Technol, Vol. 3, 2013, pp. 2025-231.