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Synthesis of Carbon Nanostructure using Cu-Ag Nanocatalysts by Spray Pyrolysis Technique

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Abstract: ***Multiwalled carbon nanotubes (MWCNTs) were synthesized by a simple spray pyrolysis technique at an optimum temperature of 700°C using turpentine oil as the source of carbon. Ar was used as the carrier gas to generate the turpentine mist and Ag-Cu nanoparticles were used as the catalyst. The morphological structures of the MWCNTs were investigated by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and X-ray diffraction pattern. A mixture of Ag and Cu nano catalyst increases the yield of MWCNTs than pure Ag nano catalyst.***

Keywords: Multiwalled carbon nanotubes, turpentine oil, spray pyrolysis.

1. Introduction

Carbon nanotube (CNT) becomes an important material on nanoscale science and technology. CNT has a large surface area that provides plenty of sites for its good adsorption. The large surface area enhances the chemical reactivity of carbon nanotubes. Lead can cause serious disorder (anemia, kidney disease, mental disorder) in human body. In addition to the cancer, dioxins adversely affect the immune and endocrine systems and the development of fetuses [1]. Dioxins are mainly generated from the combustion of organic compounds in waste incinerators, such as municipal waste, medical waste, hazardous waste, and army stockpiles (chemical agents). The high chemical reactivity and high stability of CNTs are becoming more effective for Pb removal for water purification and is more effective than commonly used activated carbon [2, 3]. The capability of fluoride and dioxin removal of CNTs is also superior to activated carbon [1, 4]. It is reported that after modification MWCNTs are also effective for adsorption of hydrated ions i. e effective for seawater desalination [5]. Srivastava et. al. [6] fabricated cylindrical membranes water filter having radially aligned carbon nanotubes walls, with diameters and lengths up to several centimeters, which is effective for the elimination of multiple components of heavy hydrocarbons from petroleum as well as filtration of bacterial contaminants (such as Escherichia coli or the nanometre-sized poliovirus) from water.

In this work, we have developed carbon nanostructure using turpentine oil by spray pyrolysis technique [7]. The nano structural growth is catalysed by a mixture of Cu and Ag nanoparticles with different weight ratio. Ar is used as the carrier gas to generate the turpentine mist in the nebuliser. All the synthesis was done at an optimum temperature of 700°C. Carbon nanotubes have been fabricated using different catalysts like Fe, Co, Ni, Ag, Au, Pt, Cu, Pd etc [7-10]. But no report has been found on formation of carbon nanotubes by Ag-Cu catalyst.

2. Experimental

Carbon nanotubes (CNT) are synthesized by a simple spray pyrolysis technique using turpentine oil as a natural source of carbon. Ar is used as the carrier gas to generate the turpentine mist in the nebulizer. The CNT growth is catalyzed by a mixture of Cu and Ag nanoparticles with different weight ratios. The quartz tube was flushed by Ar gas for 10 minutes to remove the air from the quartz tube and also to create an inert atmosphere before heating the reaction furnace. The reaction furnace was heated to the temperature 700°C. As the furnace reached the desired temperature, the turpentine oil was passed slowly through the spray nozzle by opening the control cock. In spray pyrolysis techniques, vaporization and pyrolysis of carbon sources occur simultaneously. Ar is used as the carrier gas to generate the turpentine mist in the nebulizer. The flow of turpentine oil was continued for 10 minutes. After the deposition, the chamber was cooled down to room temperature in the presence of Ar gas flow. The sample was collected from the quartz boat after cooling.

3. Results and Discussions

The variation of Ag and Cu nanocatalyst mixture by different weight ratios on the synthesis and properties of carbon nanoparticles was studied in detail. The CNTs were analyzed by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray diffraction.

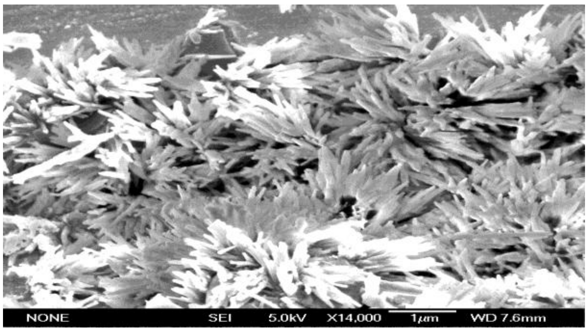


Figure 1(a)

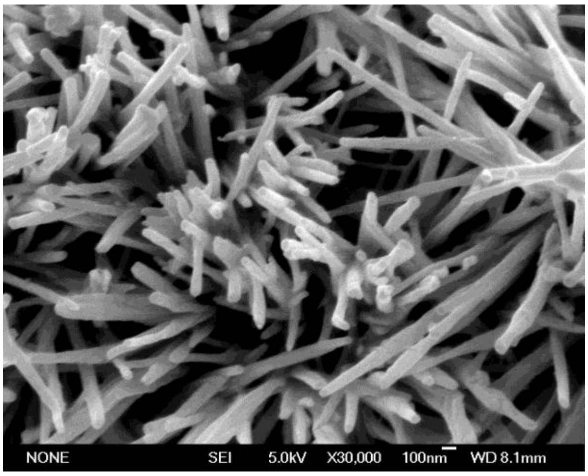


Figure 1(b)

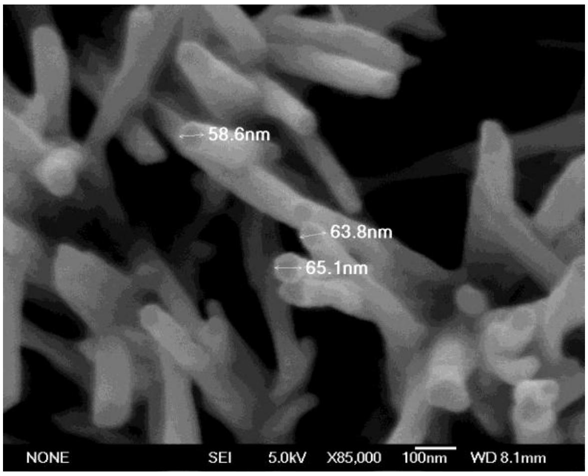
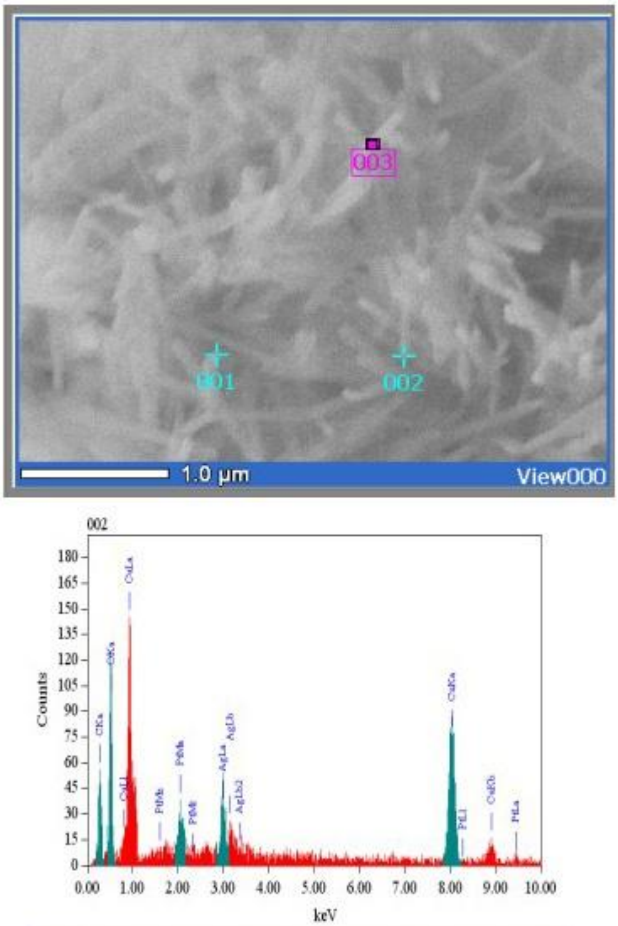


Figure 1(c)

Figure 1: SEM micrograph of carbon nanotubes synthesized using (a) pure Ag catalyst (sample # 1), (b) & (c) a mixture of Ag and Cu nano catalyst (sample # 2), but at different magnification.

Figure 1a shows the morphology of the synthesized carbon powder using pure Ag catalyst (sample # 1), investigated by Scanning Electron Micrograph (SEM). The image clearly shows the growth of highly dense cactus like structures. Introducing Cu nano particles along with Ag nano catalyst (weight ratio of Ag: Cu <1) growth of well aligned high yield CNTs are observed from SEM images in Figure 1b and 1c (sample #2). Further increase of the concentration of Cu (by weight) in the mixture of Ag-Cu nanocatalysts is not effective for the growth of carbon nano structure, as observed in SEM studies. Even pure Cu nano catalyst is also not an effective catalyst for synthesis of carbon nanostructure. Hence, the use of a mixture of Ag and Cu catalyst with less amount of Ag compared to Cu, produces CNTs with high yield.



Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation	K
C K		0.277	25.72	0.14	43.49				9.9091
O K		0.525	36.28	0.25	46.05				39.4066
Cu K		8.040	27.65	0.38	8.84				38.3197
Ag L		2.983	6.52	0.20	1.23				8.4022
Pt M		2.048	3.83	0.30	0.40				3.9623
Total			100.00		100.00				

Figure 2: EDX spectrum on a carbon nanotube of sample # 2

The Energy Dispersive X-ray analysis (EDX) spectrum of the sample # 2 in Figure 2 confirms that the nanostructure is mainly consists of carbon. The presence of Cu and Ag catalysts in the CNTs are also confirmed. For SEM & EDX studies Pt coating is used on the sample. As the Pt-sputtering is done in air, some oxygen is observed in EDX.

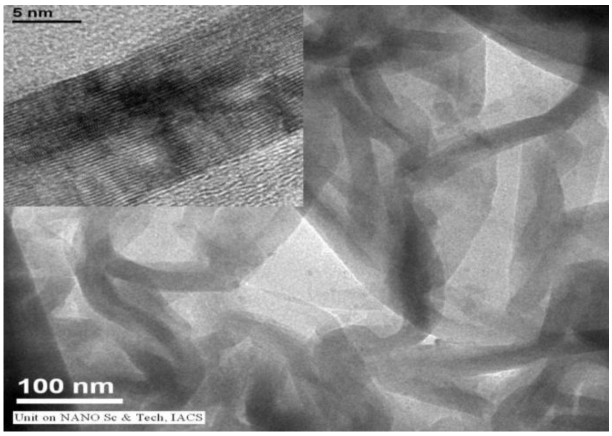


Figure 3: TEM micrograph of sample # 2, the inset shows the HRTEM micrograph

Figure 3 shows the Transmission Electron Micrograph (TEM) of sample # 2, prepared with weight ratio of Ag to Cu < 1. The nanotubes are of ~ 30 nm outer diameter. The inset picture is the High Resolution Transmission Electron Micrograph of a carbon nanotubes. The picture clearly shows the formation of multiwalled carbon nanotubes (MWCNTs) of ~ 15 nm outer diameter. These carbon nanotubes are basically solid fiber of carbon.

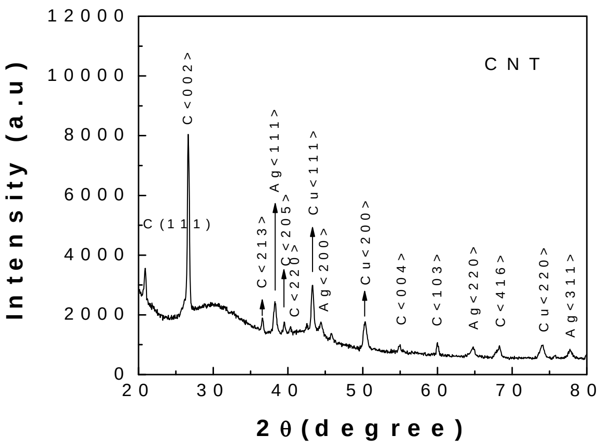


Figure 4(a)

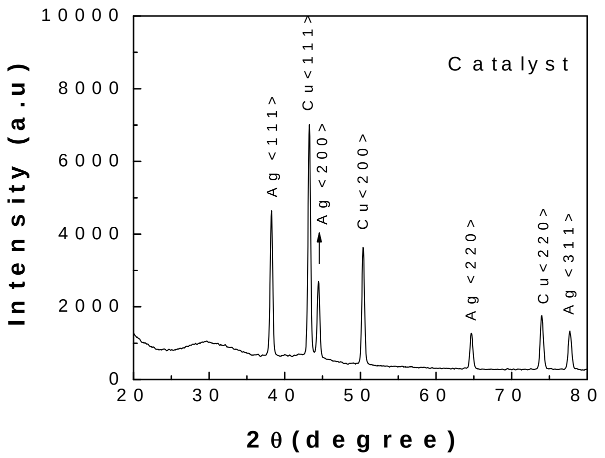


Figure 4(b)

Figure 4: X-ray diffraction pattern of the (a) synthesized carbon nanotubes (sample # 2) and (b) catalyst (mixture of Ag and Cu nano particle) used for synthesis of sample # 2.

X-ray diffraction pattern of sample # 2 and its corresponding catalyst are shown in Figure 4a and 4b respectively. Highly oriented graphite carbon structure along <002> direction is indicated by the peak around 26^o (2□) in the CNTs, as shown in Figure 4a (JCPDS 23-0064). Presence of <101>, <004>, <103>, <110> peaks of graphite in the CNTs are also identified along with <111>, <213> and <416> planes of Chaoite carbon with much lower intensity compared to graphite carbon. Zhang et. al. also observed <002> plane of graphite carbon as the most dominating peak along with other graphite peaks with very low intensity [5]. In the catalyst of the sample # 2, <111>, <200>, <220> and <311> planes of Ag and <111>, <200> and <220> planes of Cu are present in the X-ray diffraction pattern, as shown in Figure 4a. Theses planes are also present in X-ray diffraction pattern of carbon (Figure 4b) with much lower intensity compared to the <002> planes of graphite carbon.

It is well known that Fe, Co and Ni have the catalytic function of graphite formation [11]. Jean – Yves Raty et. al reported that the binding of a carbon atom to the Fe-family metal cluster (Fe, Co, Ni) is much larger than Au and the binding energy of graphene like fragments is also very small for them [12]. The same picture is applicable to Ag and Cu noble metal. Therefore, carbon atoms can not stay on noble metal particles for a time long enough for tube formation, whereas it is much easier for Fe family metal [12]. Daisuki et al. reported that pure Ag, Cu, Au nano particle (≤3 nm) have the catalytic function of graphite formation and forms Single Walled Carbon Nanotubes (SWCNTs) like Fe family elements (≤3 nm) by Chemical Vapour Deposition technique [10]. Their explanation is that carbon atoms are soluble in metal clusters and carbon atoms might precipitate to cover the surface of the nanoparticle and forms the precursor of nano tubes growth. In our studies, it is observed that pure Ag nanocatalyst initiates growth of carbon nano structure in multiple directions and form cactus like structure. On the other hand, a mixture of Ag and Cu nanocatalyst (Ag: Cu <1) grows straight aligned MWCNTs with ~ 15 nm outer diameters, observed from HRTEM studies. The tubes are solid fiber of carbon. The X-ray diffraction confirms the MWCNTs are mostly graphite structure with <002> orientation. This may be explained as follows. Both Ag and Cu have a single S electron outside a completed d shell, however the stability of Cu is less than that of Ag. In case of pure silver catalyst the growth in multiple direction is terminated due to small covalent bonding between a single C and a catalyst surface, and negligible graphene adhesion energy of the sp^2 bonded C on catalyst. On the other hand, Cu-Ag nanocluster enhances the number of covalent bonding between a single C and a catalyst surface and graphene adhesion of the sp^2 bonded C on catalyst is improved due to increase of chemical reactivity of Cu-Ag nanoclusters compared to pure Ag clusters. Hence C atoms are bound to the Cu-Ag metal particles for a long time to form stable carbon nanotubes.

4. Conclusions

Multiwalled carbon nanotubes (MWCNTs) are synthesized using the spray pyrolysis technique. A mixture of Ag and Cu nanocatalyst under a particular weight ratio (Ag: Cu <1) is effective for the growth of well-aligned MWCNTs with an outer diameter of ~ 60 nm, as observed from the SEM micrograph. The TEM micrograph shows nanotubes of ~ 15 nm inner diameters. The tubes are the solid fibre of carbon. The X-ray diffraction confirms the MWCNTs are mostly graphite structures with <002> orientation.

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