Growth of Carbon Nano-Tubes from Electric-Arc-Furnace Dust Directly

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A green process has been successfully developed to mass-produce carbon nano-tubes (CNTs) using electric-arc-furnace (EAF) dusts as the catalyst. The CNTs were prepared by a thermal CVD process with a gas mixture acetylene and nitrogen blown directly on the EAF dust that was firstly treated by a reduction period. Preliminary experimental results illustrated that CNTs were easily synthesized in large quantity and in curly shapes. The characteristics of as-grown CNTs were evaluated by transmission electron microscopy and Raman spectrometry to be of good graphitic structure. This production method is extremely meaningful both environmentally and industry-wise.

1. Introduction

Electric arc furnace (EAF) dust is a major by-product waste generated by secondary steelmaking industries (mini-mills) and is a source of notorious air pollution to the nearby areas of the steel mills. The dust is a complex, fine-grained, high-density material, containing significant amounts of zinc and iron together with variable amounts of calcium, lead, nickel, cobalt, cadmium, etc., depending on the type of steels produced. In typical EAF operation, approximately 1–2% of the charge is converted into the dust. Currently, over 700,000 tons of EAF dusts are produced each year in USA and Canada. The tonnage is one order of magnitude more worldwide. EAF dust has been classified as hazardous waste in most regions of the world. It is not allowed dispose in regular landfill sites because of the susceptibility of the heavy metals, particularly lead, chromium and cadmium, those will be leached into the environment. Therefore, tremendous efforts have been bestowing to tackle the EAF dust problems. The currently studied treatment methods include the following: high temperature metal recovery (HTMR) processes (mainly of zinc metal), hydrometallurgical processes, plasma processes, vitrification methods and chemical stabilization.\(^1\)

Most high temperature (including plasma) recovery operations for metallic zinc from the industrial EAF dust have had problems during zinc condensation stage mainly due to the re-oxidation of zinc vapour with carbon dioxide. Previous researchers had indicated that the predominant mineralogical phases of EAF dusts are iron spinels, magnetite (FeO·Fe\(_2\)O\(_3\)), zinc ferrite (ZnO·Fe\(_2\)O\(_3\)) and jacobite (MnO·Fe\(_2\)O\(_3\)), solid solutions of those three spinels, zincite (ZnO) and fayalite [(FeO\(_2\)·SiO\(_2\)].\(^2\) The EAF dust particles are, generally, less than 1 \(\mu\)m in size, some even less than one-tenth of a micro-meter.\(^3\) To the current authors, all of these characters are very suitable for the catalytic growth of carbon nano-tubes (CNTs). We designed to make use of such a waste as a pollution-free and high quality catalyst.

Since their first discovery in 1991,\(^3\) carbon nano-tubes (CNTs) have been one of the most actively studied materials. The remarkable structural, electrical and mechanical properties of CNTs have ignited many potential applications,\(^5\) such as field emission sources, nano-scaled electronic devices, electrode materials for batteries and scanning probes, among others, for a decade. Various methods to synthesize CNTs have been developed including arc discharge,\(^8\) vaporization using laser,\(^9\) pyrolysis and chemical vapor deposition of hydrocarbons.\(^10\) Among these, up to now, transition metal, Fe, Ni and Co and their alloys were necessarily used as a catalyst metal for the growth of CNTs by CVD processes.\(^11\) The preparation of substrates with a suitable catalyst is very essential to ensure success. The peculiar ability of the mentioned catalytic metals to form graphitic carbon layers has been thought to arise from the combination of different factors. These include the catalytic activity towards the decomposition of carbon compounds, the possibility to form unstable carbides and finally, the rapid carbon diffusion in the metallic particles. The properties of a catalyst, including size, porosity and nature of metallic materials, influence the growth results of CNTs.

In this work, we used EAF dust as the catalyst for the growth of CNTs by thermal chemical vapour deposition (CVD) method. The characteristics of as-grown CNTs were checked by SEM, TEM and Raman analysis.

2. Experimental

In our method, the growth of CNTs was performed using a thermal CVD system. The EAF dusts obtained from a steel-mill in Taiwan were ground to break the agglomeration and put into a quartz boat then transferred to the CVD chamber. The chamber was pumped down to less than \(\sim 10^{-3}\)Torr using a mechanical pump. There were two stages in the growth procedures. Firstly, the reduction stage, the dust samples were reduced at 550 °C under a flow of 9%H\(_2\) in N\(_2\) (flow rate of H\(_2\) + N\(_2\) 100 sccm) keeping at 2.4 × 10\(^4\) Pa for more than one hour. Secondly, the growth stage, a mixture of acetylene (C\(_2\)H\(_2\)) and nitrogen (N\(_2\)) was introduced into the chamber at a total flow rate 100 sccm for 30 min. The chamber pressure, temperature and volume ratio of C\(_2\)H\(_2\)/N\(_2\) were optimized at 180 Torr, 700 °C and 30/70, respectively. During heating and cooling periods, the samples were kept in N\(_2\) atmosphere.

To investigate the grown CNTs, scanning electron microscopy (SEM, Hitachi 3500H), transmission electron microscopy (TEM, JEOL, JEM-3010) and Raman spectrometry (RENISHAN 1000B) were used.
3. Results and Discussion

Figure 1 shows the typical scanning electron microscope (SEM) morphology of the EAF dust. The shape of EAF dust particles was almost spherical and the size distributes from 2 μm to 10 nm.

Figure 2 displays SEM images of CNTs grown on reduced EAF dust at 700°C for 30 min using a mixture of C₂H₂/N₂. It can be seen that the growth of CNTs extends to a relatively large area on the surface of reduced dust particles [Fig. 2(a)]. Their morphology looks like the surface of “rambutan”. Higher magnification image [Fig. 2(b)] shows that they are entangled and curly in shape. From the literature it has been known that porous substrates with nanometer sized iron particles were necessary for the growth of CNTs by thermal CVD process. An XRD pattern of the EAF dust used in this research is shown in Fig. 3. The major peaks in the pattern indicate that the EAF dust contains significant quantities of zinc oxide (ZnO), the zinc ferrite (ZnO·Fe₂O₃) and copper silicate (CuO·SiO₂). During reduction period, zinc oxide was reduced to zinc metal and vaporized leaving macro- to micro-porosity in the reduced dust. At the same time, zinc ferrite spinel was reduced to nano-size iron. These freshly reduced nano iron particles served as highly active catalyst and suitable nucleation sites for the decomposition of hydrocarbon gas and the growth of CNTs.

Transmission electron microscope (TEM) bright-field images of an as-grown specimen reveal a mixture of CNTs [Fig. 4(a)] and carbon nano-fibres [CNFs, Fig. 4(b)]. The catalyst can be seen to stay on the tip of CNTs as shown in Fig. 4(a).

Figure 5 shows images of CNTs grown on the dust obtained from a vacuum induction melting (VIM) furnace that is used for refining super-alloys in Taiwan. The morphology of CNTs is different from that grown on EAF dust. The CNTs grown on VIM dust are straighter and coarser in diameter than those on the EAF dust [Fig. 5(a)]. Some of them screw closely as helical carbon nano-ropes (CNRs) as shown in Fig. 5(b). Figure 5(c) shows a TEM micrograph of helical CNRs.

Raman spectroscopy [Fig. 6] of as-grown specimens on EAF and VIM dust shows two broad band peaks centred at 1349 (the D band) and 1588 cm⁻¹ (the G band), respectively. The ratio of the intensities between the D to G Raman bands is usually expected to be small for purified CNTs. In our cases, a large amorphous carbon background signal is manifest because of the direct use of EAF or VIM dust that contains many impurities. However, the position and the well-defined shape of the D and G peaks point to a well-structured graphitic morphology in the as-grown CNTs.
4. Conclusions

In conclusion, a green process has been developed to mass-produce CNTs by making use of EAF or VIM dust, a major by-product of steelmaking industries and a headache pollution source. The preliminary experimental results presented here shows that the EAF dust can be used as the catalyst for the growth of CNTs, CNFs or CNRs by thermal CVD process. The yield of CNTs can be improved if the growth parameters and pretreatment of EAF dust will be further optimised in depth.
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REFERENCES


Fig. 6 Raman spectra of CNTs samples grown on EAF and VIF dust.