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A Systematic and Comparative Study of Binary Metal Catalysts for Carbon Nanotube Fabrication Using CVD and Laser Evaporation

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Systematic studies to investigate binary catalysts combining the well-established standard transition metals Fe, Co and Ni with less used metals such as Al, Pb, Dy, Gd, Ga and Zn were explored in supported catalyst chemical vapor deposition. The findings show different carbon nanostructures can be obtained depending on the choice of catalyst mix. Comparative studies with Al as a co-catalyst with Fe or Co or Ni were explored in a laser evaporation reactor in both a pure nitrogen environment and a nitrogen environment with additional hydrogen present. The addition of hydrogen etches amorphous carbon leading to cleaner samples. In terms of the obtained carbon nanostructures, the variations among the different binary catalysts were the same for both synthesis routes investigated.

Keywords Carbon nanotubes, chemical vapor deposition, laser ablation, Raman spectroscopy, transmission electron microscopy

Introduction

Carbon nanotubes have numerous promising properties (e.g., mechanical, electronic and thermal properties) (1–4) and therefore are the subject of intense investigation due to their many potential applications such as nanometer-scale electrical devices, gas storage media, nanotweezers, structural composites, nanoelectronics and biological sensors (5–9).

Various techniques for CNT synthesis are possible, including electric arc-discharge, laser evaporation and chemical vapor deposition (CVD) as the most commonly implemented routes (10–13). Synthesis using CVD is the most popular route due to its scale-up
potential and simplicity. CVD typically involves growth in the presence of transition metal catalyst nanoparticles.

There are many reports in the literature showing the high catalytic activity of Fe, Ni, Co and their alloys for carbon formation (14–16) and the effective synthesis of carbon nanotubes (17–19). The use of metal alloys as catalysts (Fe/Ni, Ni/Co, Fe/Co) allows greater control over the nanotubes diameters, purity and type (SWCNT, DWCNT, MWCNT) (20–22). Few studies have been conducted to evaluate the formation of Fe, Ni and Co alloys with non-standard metals (e.g., Zn, Dy, Pb) as catalysts for the synthesis of carbon materials. A few preliminary studies hint that non-standard metals and alloys could indeed yield carbon nanotubes (12,23–27). Non-metal catalyst systems and catalyst free systems are also possible (28–34).

In this work, binary catalyst systems combining the traditional transition metals Fe, Co and Ni with unconventional metals such as Al, Dy, Gd, Ga, Pb and Zn are systematically explored to evaluate their potential for carbon nanostructure formation.

**Experimental**

**Chemical vapor deposition**

For the synthesis reactions ethanol was used as the carbon feedstock throughout. Pure magnesia powder (Alfa Aesar, 99.99%) was used as the support material. The precursors for the metals used to form the binary catalysts were all from the acetylacetonate family. The iron, cobalt and nickel precursors were provided as acetylacetonates: iron (III) acetylacetonate (Sigma Aldrich, 99%), cobalt (III) acetylacetonate (Sigma Aldrich, 99%) or nickel (II) acetylacetonate (Merck, 98%). The poor metals precursors were aluminum acetylacetonate (Merck, 98%), gallium (III) acetylacetonate (Sigma Aldrich, 99%), lead acetylacetonate (Sigma Aldrich, 99%) or zinc acetylacetonate (Sigma Aldrich, 99%), and mixed with lanthanides precursors: dysprosium acetylacetonate (Sigma Aldrich, 99%) and gadolinium acetylacetonate (Sigma Aldrich, 99%). In the case of single catalysts (for comparison) a molar ratio of X to MgO of 2:60 was used (where X represents Fe, Co or Ni). For the binary catalysts the ratio of X to Y to MgO was 1:1:60 where X = Fe, Co or Ni and Y = Al, Dy, Gd, Ga, Pb or Zn. The protocol for the reaction mixtures was as follows: Magnesium oxide powder was added into solutions of each acetylacetonate in acetone, and then the mixtures were dispersed for 30 minutes in an ultrasonic bath at room temperature. Afterwards, the suspensions were dried on a hot plate at 100°C using a magnetic stirrer. The resultant products were ground in a ceramic mortar to form homogeneous catalyst precursor mixes in powder form. The as-prepared catalyst mixture was then placed at the center of a purposely built horizontal tube furnace. Once the reaction mixture had been loaded, the reaction tube was evacuated (~10^{-3} mbar) and then heated to the desired temperature (800°C). At this point dynamic ethanol vapor (60 mbar) was introduced to the reactor. The reaction was run for 15 minutes. The system was then allowed to naturally cool down to room temperature in vacuum.

**Laser ablation**

The materials were produced by using a previously established laser ablation (LA) technique (35). The binary catalyst mixtures used were Fe:Al, Co:Al and Ni:Al at a ratio of 1:1 (pure metal powders were used). They were then mixed with high purity graphite (99.99%) so that the catalyst content formed 10wt% of the target. Both pure nitrogen and nitrogen
with a 5% hydrogen addition were used as buffer gases. The process temperature was 800°C.

Characterization

The morphological studies of the samples were carried out on a high-resolution transmission electron microscope (HRTEM)–Philips Tecnai F30 operating at 300 kV. Raman measurements were performed using an excitation laser output of 532 nm (2.33 eV) with a DXR Raman ThermoFisher spectrometer.

Results and Discussion

Table 1 presents details of all the different experiments in which standard transition metals (Fe, Co, Ni) combined with non-standard metals (Al, Ga, Pb, Zn, Dy, Gd) as binary catalyst systems are investigated. For the synthesis of the carbon nanomaterials, two methods where used and the results compared. The two methods used were CVD and LA.

Figure 1 presents a selection of representative TEM micrographs of the samples produced using the CVD route. In the left column, micrographs of CNT obtained with the traditional mono-catalyst systems (Fe, Co and Ni) are provided. In all three cases multi-walled carbon nanotubes (MWCNTs) are obtained and often metal catalyst material is found in the core of the as-produced tubes. When mixing other metals into the three primary catalysts (Fe, Co and Ni) to form a binary catalyst, a variety of variations are observed. In some samples no carbon nanotubes were observed with only metal catalyst particles encapsulated in graphite being present (e.g., Fe:Pb:MgO). In other cases, graphitic sheets with encapsulated particles mixed in can be observed (e.g., Ni:Ga:MgO). In a few samples only amorphous carbon and catalyst material were present (e.g., Co:Ga:MgO). Some of the binary catalyst systems yielded carbon nanotubes; of these, some consisted mainly of single-walled carbon nanotubes (SWCNTs) (e.g., Co:Gd:MgO), while others contained mostly double-walled carbon nanotubes (DWCNT) (e.g., Ni:Zn:MgO) or MWCNTs (e.g., Fe:Ga:MgO). Greater detail of the types of structures obtained for all samples investigated is provided in Table 1. The data highlight how one can tailor the type of nano structure simply through catalyst choice for a given set of CVD synthesis parameters.

Raman spectroscopy is a powerful tool with which to investigate carbon nanotubes. The Raman spectra of carbon nanotubes are characterized by three main signals: the G-band, the D-band and a radial breathing mode (RBM). The G-band appears at around 1591 cm$^{-1}$ and is ascribed to the tangential modes of a graphene sheet. The D-band at around 1293 cm$^{-1}$ is related to the defects in a graphene sheet and to the presence of amorphous carbon. The RBM peaks originate from the tubes expanding and contracting as if breathing. Due to the spectrometers notch filter usually only carbon nanotubes with diameters narrower than 2.0–2.5 nm are measureable; hence, RBM signatures usually arise from SWCNTs. The position of RBM mode is inversely proportional to the carbon nanotubes diameter (36–40). In this study the diameter “d” of SWNT was estimated from the RBM Raman shift $\nu$ using the relationship $d/\text{nm} = 248/(\nu/\text{cm}^{-1})$ (39). The Raman spectroscopic data suggest the presence of SWCNT in samples, for example, in Co: Dy: MgO, Ni: Mg: O and Ni: Zn: MgO (see Figure 2), which show RBM peaks between 145 and 280 cm$^{-1}$. In some samples (see Table 1) RBM were not observed. Details of the RBM modes found or not found for all examined samples are provided in Table 1. The diameter distribution of the CNT determined according to the observed RBM signature.
Table 1
Details of all the experiments preformed using CVD and laser evaporation. The different catalyst materials and information on the resultant material are provided

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter From RBM [nm]</th>
<th>G/D</th>
<th>SWCNT</th>
<th>MWCNT</th>
<th>FILLING</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical vapor deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe:MgO</td>
<td>NONE</td>
<td>0.53</td>
<td>–</td>
<td>MOSTLY</td>
<td>SHORT AND LONG</td>
</tr>
<tr>
<td>Fe:Zn:MgO</td>
<td>NONE</td>
<td>0.37</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe:Ga:MgO</td>
<td>NONE</td>
<td>0.56</td>
<td>–</td>
<td>MOSTLY</td>
<td>SHORT</td>
</tr>
<tr>
<td>Fe:Pb:MgO</td>
<td>NONE</td>
<td>0.43</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe:Gd:MgO</td>
<td>NONE</td>
<td>0.48</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe:Dy:MgO</td>
<td>NONE</td>
<td>0.48</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe:Al:MgO</td>
<td>NONE</td>
<td>0.36</td>
<td>–</td>
<td>ONLY</td>
<td>LONG</td>
</tr>
<tr>
<td>Co:MgO</td>
<td>NONE</td>
<td>0.38</td>
<td>–</td>
<td>MOSTLY</td>
<td>SHORT</td>
</tr>
<tr>
<td>Co:Zn:MgO</td>
<td>NONE</td>
<td>0.34</td>
<td>–</td>
<td>MOSTLY</td>
<td>SHORT</td>
</tr>
<tr>
<td>Co:Ga:MgO</td>
<td>NONE</td>
<td>0.39</td>
<td>–</td>
<td>ONLY</td>
<td>–</td>
</tr>
<tr>
<td>Co:Pb:MgO</td>
<td>NONE</td>
<td>0.36</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Co:Gd:MgO</td>
<td>0.91, 1.09, 1.22, 1.37, 1.5</td>
<td>0.54</td>
<td>A FEW</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Co:Dy:MgO</td>
<td>0.97, 1.20</td>
<td>0.41</td>
<td>VERY FEW</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Co:Al:MgO</td>
<td>0.95, 1.1, 1.55, 1.7</td>
<td>0.89</td>
<td>A FEW</td>
<td>MOSTLY</td>
<td>–</td>
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<tr>
<td>Ni:MgO</td>
<td>0.95, 1.08, 1.12, 1.34, 1.58</td>
<td>0.43</td>
<td>VERY FEW</td>
<td>MOSTLY</td>
<td>SHORT AND LONG</td>
</tr>
<tr>
<td>Ni:Zn:MgO</td>
<td>0.95, 1.12, 1.34, 1.5</td>
<td>0.62</td>
<td>VERY</td>
<td>A FEW</td>
<td>–</td>
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<td>Ni:Ga:MgO</td>
<td>NONE</td>
<td>0.4</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Ni:Pb:MgO</td>
<td>NONE</td>
<td>0.66</td>
<td>–</td>
<td>ONLY</td>
<td>SHORT AND LONG</td>
</tr>
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<td>Ni:Gd:MgO</td>
<td>1.14, 1.07, 1.28</td>
<td>0.52</td>
<td>A FEW</td>
<td>MOSTLY</td>
<td>SHORT AND LONG</td>
</tr>
<tr>
<td>Ni:GdMgO</td>
<td>NONE</td>
<td>0.46</td>
<td>–</td>
<td>ONLY</td>
<td>–</td>
</tr>
<tr>
<td>Ni:Al:MgO</td>
<td>0.9, 1.1, 1.55, 1.34, 1.8, 1.9</td>
<td>0.89</td>
<td>A FEW</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Laser ablation (N₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe:Al</td>
<td>NONE</td>
<td>0.49</td>
<td>–</td>
<td>ONLY</td>
<td>–</td>
</tr>
<tr>
<td>Co:Al</td>
<td>1.55</td>
<td>0.52</td>
<td>A FEW</td>
<td>MOSTLY</td>
<td>–</td>
</tr>
<tr>
<td>Ni:Al</td>
<td>1.55</td>
<td>0.58</td>
<td>A FEW</td>
<td>A FEW</td>
<td>–</td>
</tr>
<tr>
<td>Laser ablation (N₂/H₂)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe:Al</td>
<td>NONE</td>
<td>0.55</td>
<td>–</td>
<td>ONLY</td>
<td>–</td>
</tr>
<tr>
<td>Co:Al</td>
<td>1.55</td>
<td>0.64</td>
<td>A FEW</td>
<td>MOSTLY</td>
<td>SHORT AND LONG</td>
</tr>
<tr>
<td>Ni:Al</td>
<td>1.55</td>
<td>0.46</td>
<td>A FEW</td>
<td>MOSTLY</td>
<td>LONG</td>
</tr>
</tbody>
</table>
range from 0.9 to 1.8 nm. The quality of the samples with respect to the number of defects in the carbon walls can be estimated via the intensity ratio of G band (graphite-like in-plane mode) and D band (defect mode). The higher the value of this ratio, the higher is the quality of the sample. The G/D ratio for all samples are presented in Table 1 and visualized as a plot in Figure 3. From the data it is easy to see the highest G/D ratios arise for samples obtained with the Ni:Al:MgO catalyst and the lowest G/D ratios for samples obtained with the Co:Zn:MgO catalyst. No clear trend between catalyst mixes is observed.

In order to be more complete with our study of standard and non-standard metal catalysts, their use within laser ablation CNT synthesis was investigated. Fe, Ni and Co combined with Al where used due to the higher quality of these samples in the CVD. In addition, these Al based binary catalyst systems were run in a pure nitrogen environment as well as in a nitrogen/hydrogen mix. For easy comparison, representative transmission electron microscopy (TEM) images for the CVD prepared samples are provided with the laser evaporation prepared samples both in pure N$_2$ and N$_2$/H$_2$ atmospheres. These are
Figure 2. Representative Raman spectra of samples produced by CVD method using: CoDyMgO, NiMgO, NiZnMgO and FeGaMgO catalysts (color figure available online).

Figure 3. The intensities of G/D ratios for all samples produced by CVD (color figure available online).

provided in Figures 4, 5 and 6 for a binary catalysts mix of Al with Fe, Co and Ni, respectively. These TEM micrographs show that all samples prepared using laser evaporation in a pure N$_2$ environment have noticeably higher amounts of amorphous carbon and have structurally rather disordered carbon nanotubes. In the case of Al being mixed with Co and Ni a few SWCNT are also present. The data suggest H$_2$ etches amorphous species and so leads to cleaner samples.

For comparison, the Raman spectra for the samples shown in Figures 4, 5 and 6 are given in Figure 7. The data show some clear trends for the catalyst mix across both the CVD and laser evaporation route. In the case of Al mixed with Fe, no SWCNT are observed in the TEM studies and also in the Raman spectra. Al when mixed with Co or Ni does lead
to some SWCNT being produced in the sample. This difference may be due to Fe alloys having higher carbon solubilities than their Co or Ni alloy counterparts. In the case of Al mixed with Co and Ni, there are obvious differences in the RBM modes when comparing LA produced samples with those grown from CVD. When using LA the narrower RBM range as compared to that found with the CVD synthesized samples suggest a narrower diameter distribution for the LA grown SWCNT. Generally it is well known that laser ablated samples lead to SWCNT with narrow diameters (12,17,41), and this study is in keeping with this. However, LA samples generally lead to samples containing CNT with only a single wall, viz. SWCNT. This is argued to be so due to the catalyst volume to surface area model (41). In this model it is assumed a hemispherical cap is required upon nucleation. This cap forms as carbon precipitates from the catalyst particle upon cooling.
and approaching its eutectic temperature. However, as the catalyst volume increases so does the carbon available and at some point the available carbon precipitating exceeds that required for a hemispherical cap and the catalyst particle is then simply encapsulated with graphite. This mechanism also explains the narrow diameter distribution of the obtained SWCNT. The sample model can be used to explain the formation of MWCNT in CVD with supported catalysts because when a catalyst is supported as it gets bigger the excess carbon cannot encapsulate the particle due to the support/particle interaction. The excess carbon simply forms further caps within the first cap formed. Hence as the particle gets bigger so do the number of caps and hence tube walls (41,42).

However, in this study we observed a mix of both MWCNT and SWCNT present in the laser evaporation samples. Both the above arguments can explain this behavior as
follows: Upon ablation there will be a catalyst mix with particles having different ratios of the two metals. These differing alloy mixtures will precipitate their carbon at different points in time and have differing carbon supplies due to variations in carbon solubility and size. Some of these particles will lead to SWCNT, some will be encapsulated with graphite and others will simply freeze. Other particles, while still molten, may collide with a larger frozen particle which in essence acts as a support. Thus, now the supported catalyst can produce a MWCNT since the effective support blocks encapsulation by carbon. This process is similar to that described previously by us (12). The presence of MWCNT in the samples can degrade the G/D ratio found in the Raman spectra. Thus the G/D ratios for the LA samples are similar to those obtained from the CVD process as shown in Figure 8.
Conclusion

A variety of non-standard metals (e.g., Al, Gd and Pb) in combination with three well-established transition metal catalysts, namely Fe, Co and Ni, were systematically explored as catalyst systems for the synthesis of carbon nanotubes using CVD. While the data show different carbon nanostructures can be obtained by changing the catalyst type and mix, no clear pattern to explain the result and products could be established.

The specific case of Al mixed with a primary metal (Fe, Co or Ni) was explored across both CVD and laser ablation synthesis. In all cases the inclusion of Fe in the catalyst mix yielded only MWCNTs. Samples containing Co or Ni led to a mix of MWCNT and SWCNT. The formation of these CNT can is explained through a previously developed model for CNT growth, namely, the catalyst volume to surface area model.
In the case of laser evaporation, the inclusion of hydrogen was also explored and was found to significantly reduce amorphous species, and hence, plays a positive role.

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References

