CO-CU POWDERS FOR THE PRODUCTION OF COMPLEX CARBON NANOSTRUCTURES: MW-CNT DECORATING WRINKED CARBON BELTS

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Introduction

Three dimensional hybrid structure are being developed as an alternative to combine the structural benefits of graphene, CNTs, wrinkled graphene, and fullerenes[1] into one framework to be used in different applications such a free-metal catalyst[2], electrode for ion-Li batteries[3], sorbent for environmental remediation[4] or as electrode for redox-reaction catalyst[5]. The present investigation relays on the formation of wrinkled carbon belts structures that works as framework for the growing of CNT over its surface using a Co-Cu bimetallic mixture as catalyst. Also the temperature profile plays a role on the growing of different hybrid carbon nanostructures. These structures are doped with nitrogen, have length dimension of about ~120 μm, are magnetic and can be used as electrodes for redox-reactions.

Materials and Methods

A mixture of Co powder (99.25%, Alfa-Aesar) and Cu powder (99%, Alfa-Aesar) was done at a ratio of 10:1 respectively. A mechanical process using a ball mill equipment was applied during one hour and then were pressed using 0.1g at 10 t to obtain a tablet. For the synthesis, a quartz tube of 1.1m length and 1in diameter was used as reactor and two tubular furnaces with different temperature. Three samples of 1cm x 1cm surface were positioned at the centre of the 750 °C furnace, between two furnaces and at the centre of the 850 °C furnace. A mixture of benzylamine (49.7 % wt/wt), ethanol (49.9 % wt/wt) and thiophene (0.32 % wt/wt) works as precursor of nitrogen, sulphur, oxygen and carbon atoms and a mixture of H_2/Ar (5%/ 95%) was used as trawl gas. The process is maintained during two hours at these conditions. The hybrid carbon materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, cyclic voltammetry and physical properties measurement system (PPMS).

Results and Discussion

Figure 1a illustrates a magnified micrograph from the sample synthesized at 850 °C. Hybrid CNTs-wrinkled carbon belts (WCBs) were found at the surface. The WCBs structure has a length of about ~120 μm, ~ 4.5 μm width and ~0.5 μm thickness. CNT grows over the surface of the WCBs (**figure 1b**) and distributed over the sample. The diameter of the CNT are about 50 nm and highly curved. **Figure 1c** illustrates the structures obtained at 800 °C. The morphology changes and no trace of long WCBs is observed. Instead short defected WCBs and corrugated CNF are observed mixed with metallic nanoparticles (**figure 1d**). The WCBs has several folks creating section of the WCB. **Figure 1e** illustrates the growing of graphitic material over the Co-Cu NPs. This could be related with corrugate graphite surrounding the metallic nanoparticle.

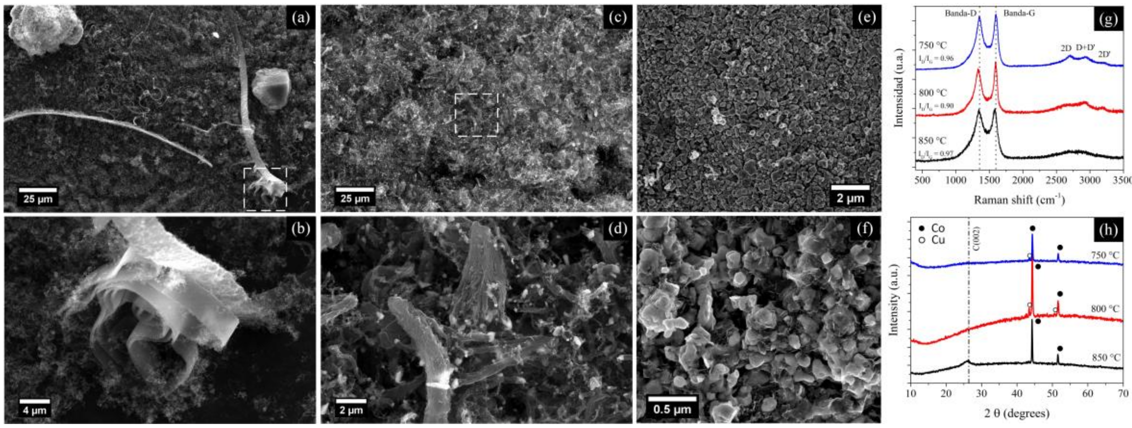

Figure 1: a-b) CNT grown over Wrinkled Carbon Belts at 850 °C. c-d) Defected wrinkled belt structure obtained at 800 °C. e-f) Cu-Co NPs surrounded by graphitic material obtained at 750 °C. g) Raman spectra of samples obtained at 750 °C, 800 °C and 850 °C. h) XRD diffraction pattern of samples obtained at 750 °C, 800 °C and 850 °C.

Figure 2g compares the Raman spectra for sample obtained at 750 °C, 800 °C and 850 °C. In the three samples were observed the D-band (~1356 cm^{-1}) and the G-band (1593 cm^{-1}). The relation I_D/I_G which is related with the degree of graphitization of the sample varies being the sample at 850 °C the one with more defects. Also second order vibration modes like 2D, D+D' and 2D' are highlighted for sample at 750 °C and can be related with the graphitic structure surrounding the Co-Cu NPs. **Figure 2b** illustrates the crystallographic changes for samples. In the case of sample at 850 °C it is visible the (002) crystallographic plane from carbon.

Conclusions

The growing of a variety of hybrid and complex carbon nanostructures were synthesized using a tablet of Co-Cu catalyst. Also the temperature has a considerable effect over the growing of different type of graphitic structures going through the synthesis of graphitic core structure (750 °C), defected WCBs (800 °C) and hybrid CNT-WCBs. This work set the tone for further research focused on the bimetallic catalytic effect in the growing of hybrid carbon nanostructures.

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References

1. Mann, S. Self-assembly and transformation of hybrid nano-objects and nanostructures under equilibrium and non-equilibrium conditions. *Nature materials* **8**, 781–792 (2009).
2. Shinde, S. S. *et al.* Scalable 3-D Carbon Nitride Sponge as an Efficient Metal-Free Bifunctional Oxygen Electrocatalyst for Rechargeable Zn-Air Batteries. *ACS Nano* **11**, 347–357 (2017).
3. Rohman, F., Azizah, U. & Prihandoko, B. Study of electrochemical performance of amorphous carbon-coated graphite for Li-ion battery. *AIP Conference Proceedings* **1823**, (2017).
4. Muñoz-Sandoval, E. *et al.* Carbon sponge-type nanostructures based on coaxial nitrogen-doped multiwalled carbon nanotubes grown by CVD using benzylamine as precursor. *Carbon* **115**, (2017).
5. Yan, Z. *et al.* Three-dimensional metal- Graphene- Nanotube multifunctional hybrid materials. *ACS Nano* **7**, 58–64 (2013).