

Metal catalyst adsorption effects in the growth of carbon nanostructures on mesoporous material

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Abstract

Mesoporous silica films were used as host for metal-based (Me = Fe, Co, Ni) nanoparticles via wet impregnation at pH = 5. A hydrogen ion beam was used to reduce the metallic oxide and hydroxides, previously detected by X-ray photoelectron spectroscopy, in metals. Chemical vapor deposition processes at three different conditions varying the acetylene-nitrogen proportion were performed on the mesoporous films decorated by different metal-based nanoparticles. The grown carbon nanostructures were characterized by high-resolution transmission electron microscopy and scanning electron microscopy. The ability to

grow carbon nanostructures decreases in the following order: Fe > Co > Ni. When pure acetylene is used, iron allows to form graphene sheets around the metal catalyst like carbon nanocapsules, whereas cobalt allows to form structures that seem to be carbon nanotubes. Nitrogen leads to control the size and shape of carbon nanocapsules for iron catalyst and avoid the growth of such carbon nanotube-like structures for cobalt catalyst.

1. Introduction

Carbon nanostructures (CNS) have attracted enormous interest in the last two decades. Different carbon geometries can be obtained from single or multi-wall nanotubes, nano-onions, nanodomes up to fullerenes and graphene sheets.^{1,2,3} However, the full control of these geometries is still open. Many factors are involved in order to establish a predetermined nanostructure. Temperature, substrate, energy of reactive species, applied bias, type of catalyst, gas composition are important processing parameters for achieving a final CNS in adequate size and shape. Indeed, a predetermined nanostructure is capable to define a material property. Among them, carbon nanotubes are been used in nanocomposites in order to reach better properties owing to its mechanical strength.⁴ Moreover, many applications have been proposed in nanoelectronic as well as in optical and magnetic devices.^{5,6,7}

Recently, some works have invoked that the self-organized substrate can tailor the geometry of CNSs due to catalysts are able to be hosted in cavities like in mesoporous materials.^{8,9} In fact, the mesoporous surface is like a nanomould for catalysts and nanostructures where the latter may grow replicating the original surface. Therefore, the control of functionalizing nanoparticles deposited on the mesoporous material is an important challenge for applications in nanotechnology.^{10,11} Taking into account the electronic filling of “d” atomic orbitals, transition metals act in different catalytic ways when CNS are grown in the same experimental conditions. In summary, a predetermined CNS can be tailored by choosing the right nanoporous array, catalyst, and processing parameters.

In this work, we report the effect of different metallic catalysts on type, size, and shape of CNS grown by chemical vapor deposition (CVD) at relative low temperature on mesoporous materials. The results have been divided in two main groups: i) the different transition metal inducing different catalytic behaviors and ii) the influence of nitrogen in the obtained carbon nanostructures.

2. Experimental

The mesoporous thin films were synthesized by combining sol-gel chemistry with surfactant templating techniques by the “evaporation - induced self - assembly” process.^{12,13} The material was obtained from the tetraethoxysilane (TEOS) derived oligomers as inorganic precursor and poly(ethylene oxide)-based nonionic surfactant Brij58 (B58) as organic template. Mesoporous films were deposited via dip-coating on silicon substrate at 1.8 mm/seg, 50% relative humidity and room temperature.¹⁴ The precursor solution was prepared in such a way that the final molar concentration was 1 TEOS: 40 EtOH: 0.008 HCl: 10 H₂O: 0.05 B58.¹⁵ This solution was aged for three days prior film deposition onto silicon wafers. After dip-coating, films were stored 24 h at 50% relative humidity and then the mesostructural resistance of films was optimizing by successive thermal treatment at 60 and 130°C for 24 h each one. The stabilized films were thermally annealed by 2 h until complete elimination of the template at 350°C in air. In these initial solution composition, coating parameters, and treatment conditions, a *Im3n* body centred cubic mesoporous thin films are obtained.¹⁵ Figure 1 shows the XRD pattern of the mesoporous film where the typical feature of a cubic mesophase is presented. Diffraction data was obtained by a Siemens D-5000 Diffractometer with CuK α radiation ($\lambda = 1.542 \text{ \AA}$) by step scanning 2θ from 1.3° to 5° with a step size of 0.02° and a step time of 1 s with 1° as incidence angle.

The deposition of the Me-based (Me = Fe, Co, Ni) nanoparticles was performed by wet impregnation from a 0.2 M Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O aqueous solutions, respectively, at pH = 5 adjusting with 0.5 M NaOH solution. The mesoporous film was immersed into the solution for 2 h at room temperature and then, rinsed first with water and then with EtOH and, finally dried at 120°C for 2 h in air.

After metal adsorption and before CVD process, the samples were transferred to the attached ultra high vacuum chamber (UHV) for X-ray photoelectron spectroscopy (XPS) analysis. Details of the apparatus are reported elsewhere.¹⁶ These spectra were obtained by

using the 1486.6 eV photons from an Al target ($K\alpha$ line) and a VG-CLAMP-2 electron analyzer. The total apparatus resolution is ~ 0.85 eV (line-width plus analyzer).

As we were reported elsewhere, functionalization by hydrogen ion beam irradiation can be performed in a high vacuum chamber with DC Kaufman ion source where the reactive beam of hydrogen ions (H_2^+) was responsible for the chemical etching of the oxygen leading to convert metal oxide and hydroxides in metal.⁸ For this reason, all samples were hydrogen functionalized for 6 min before CVD condition.

After hydrogen reduction of the Me-compounds, the CVD was conducted at a temperature of $650^\circ\text{C} \pm 20^\circ\text{C}$ and pressure of 50 Pa under three different gas compositions of $C_2H_2-N_2$ (100%, 67%, and 25% of C_2H_2 , respectively) during 45 min. The CVD process was performed in a high vacuum chamber (background pressure $< 2 \times 10^{-5}$ Pa) in order to avoid the influence of residual oxygen in carbon nanostructure grow. The structural and morphological characterization of samples in cross-section and plain-view were performed by regular and high-resolution transmission electron microscopy (HRTEM Jeol JEM-3010 ARP owing a LaB_6 emission gun operating at 300 keV) and regular and high-resolution scanning electron microscopy (FEG-SEM, Jeol JSM-6330F and Zeiss Leo 982 Gemini).

3. Results and Discussion

Figure 2 shows a transmission electron microscopy (TEM) image of a typical substrate in cross-section view used for physicochemical adsorption of metallic atoms such as Fe, Co, and Ni for posterior growth of carbon nanostructures by CVD. The substrate is a mesoporous material which has an organized structure at nanoscale (array of nanoporous with size ~ 7 nm separated by ~ 1.8 nm walls).⁹

After wet impregnation, we performed XPS analysis in order to verify the presence of metals on the surface. Figures 3 a-c show the binding energy of Fe 2p, Co 2p, and Ni 2p_{3/2}, respectively, on mesoporous material at pH=5. In all cases, the XPS spectra are in agreement with MeO_x and $Me(OH)_x$ structures owing to the strong interaction between the

surface constituted by oxide groups and the ion metals from aqueous media. The fixed pH at 5 guarantees a negative charge density on mesoporous surface which allows the physicochemical adsorption of such three metals and related species. In fact, the point of zero transference charge (PZC) for SiO_2 is 2-3.7 (in pH units).¹⁷ Moreover, our calculations taking into account the XPS spectra about the metal concentrations on mesoporous surface have shown a higher Fe concentration than Co and Ni, and for the two latter a concentration of 5 at. % was estimated. Indeed, a low Ni concentration does not allow to show clearly its $2p_{3/2}$ binding energy contribution.

Figures 4a-d show scanning electron microscopy (SEM) images in plain view of carbon nanostructures (CNS) which have grown on mesoporous material decorated with Fe after CVD process at different conditions. When pure acetylene is used, dome-like carbon nanostructures can be seen only.³ However, a deeper insight by analyzing a high-resolution transmission electron microscopy (HR-TEM) image in cross-section shows iron-based particles where graphene sheets with characteristic interplanar spacing of 0.339 nm cover the metallic catalyst as in carbon nanocapsules (see Fig. 5a). Indeed, the final surface morphology is formed by a collection of carbon nanocapsules (CNC), as well as amorphous carbon. One can stress that iron nanoparticles were moved up from the mesoporous surface due to the growth of graphene sheets. Furthermore, Fig. 5b shows the interplanar spacing for iron catalyst consistent with simple tetragonal structure ($P4_2/mnm$ space group, with zone axis parallel to $[323]$ direction – ICSD collection code 165727).¹⁸ Although such surface morphology can be seen in the three CVD conditions, long and short tubular nanostructures that seem to be carbon nanotubes (CNT) are only apparent when nitrogen is used as a constituent in the reactive gas mixture (see Fig. 5b and d). Moreover, the size and shape of CNC decreases and becomes more circular, respectively, when nitrogen is used.

Figures 6a-c show SEM images of carbon nanostructures which have grown on mesoporous material decorated with Co after CVD process at different conditions. A non-nitrogen reactive gas mixture leads to obtain relative long and short CNT with diameters of

approximately 11 nm which grow following straight lines which seem to be streets due to the mesoporous surface format. Here, the presence of nitrogen is mandatory in order to avoid the formation of any type of carbon nanostructures. It is important to remark that no presence of CNC like in the iron catalytic system is observed when nitrogen is added. We could not establish the presence of CNT by HR-TEM in cross-section due to the high dispersion of carbon nanostructures does not allow an unbiased observation with the glue used to prepare the samples.

Figures 7a-c show SEM images of carbon nanostructures which have grown on mesoporous material decorated with Ni after CVD process at different conditions. Contrary to previous mesoporous materials decorated with Fe and Co, CNTs have been obtained in isolated areas independent of the presence of nitrogen in the reactive gas mixture.

There are two main groups to analyze and discuss the results: the different transition metal inducing different catalytic behaviors and the influence of nitrogen in the carbon nanostructures in terms of growth, size, and shape. One can conclude that Fe and Co show significant difference catalytic behaviors either using or not using nitrogen in the gas mixture, whereas in the case of the Ni catalyst CNT grow independent of gas mixture.

Taking into account non-nitrogen in the gas mixture, iron induces the formation of CNC in spite of such nanostructures be irregulars and big. Contrary to iron, cobalt only induces the CNT formation (longs and shorts) instead of CNC or circular structures. Moreover, a lower CNT density is obtained than those grown by using iron as catalyst. Finally, although CNT are detected when nickel is used as catalyst, they grow in an isolated way.

When nitrogen is used in the gas mixture, the CNS grown on iron seem to be smaller and with well-defined circular shapes. In fact, nitrogen bends and curls graphitic planes allowing to reach curves which can develop circular and spherical shapes.^{19,20} However and in our experiments, nitrogen avoids the formation of CNS on cobalt and nickel catalysts. We suggest that a combination of low temperature, slow kinetic due to the presence of nitrogen,

and low metal concentration may suppress the growth of CNS. In similar experimental conditions, nickel leads to increase the degree of graphitic disorder instead of organized graphene sheets.²¹ Finally, the hydrogen functionalization process is particularly interesting in the catalytic effect of transition metals where the oxidation state is the main parameter in the CNS growing process.^{22,23}

4. Conclusions

Metal-based (Me = Fe, Co, Ni) nanoparticles were absorbed via wet impregnation at pH=5 on mesoporous material. X-ray photoelectron spectroscopy shows that metallic oxides and hydroxides were obtained after adsorption. After reduction by hydrogen ion beam irradiation, carbon nanostructures were grown by chemical vapor deposition at three different conditions varying nitrogen content in the gas mixture where acetylene was used as carbon source. According to the carbon nanostructures two main groups are obtained: i) the different transition metal inducing different catalytic behaviors and ii) the influence of nitrogen in the obtained carbon nanostructures. Iron catalyzes the formation of CNC, whereas cobalt yields structures which seem to be carbon nanotubes as main nanostructures when pure acetylene was used. In all cases, nitrogen changes the sizes and shapes of CNS for iron and avoids the growth of nanotube-like structures for cobalt. In the case of nickel, the growth of isolated nanotubes can be attributed to low catalyst concentration on mesoporous surface as well as the low processing temperature.

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of the LME/LNLS (Campinas-Brazil).

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FIGURE CAPTIONS

Figure 1: XRD pattern of the mesoporous film used as substrate. The typical feature of a cubic mesophase is apparent.

Figure 2: TEM image in cross-section view of mesoporous structure used as substrate.

Figure 3: (a) Iron 2p, (b) cobalt 2p, and (c) nickel 2p_{3/2} core level binding energies for mesoporous films after wet deposition at pH=5 obtained by XPS.

Figure 4: SEM images of carbon nanostructures which have grown on mesoporous material decorated with Fe after CVD process at three different gas compositions of C₂H₂-N₂: (a) 100%, (b) 67%, and (c) 25%. (d) HR-SEM image displaying a detail of small dome-like and short nanotubes carbon nanostructures.

Figure 5: (a) High-resolution transmission electron microscopy images in cross section of mesoporous material decorated with Fe after CVD using only acetylene as reactive gas where a group of carbon nanocapsules and (b) a detail of one of them are shown.

Figure 6: SEM images of carbon nanostructures which have grown on mesoporous material decorated with Co after CVD process at three different gas compositions of C₂H₂-N₂: (a) 100%, (b) 67%, and (c) 25%.

Figure 7: SEM images of carbon nanostructures which have grown on mesoporous material decorated with Ni after CVD process at three different gas compositions of C₂H₂-N₂: (a) 100%, (b) 67%, and (c) 25%.
