A SINGLE STEP PROCESS FOR THE SIMULTANEOUS PURIFICATION AND OPENING OF MWNTs

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Introduction

The main synthesis routes of multi-walled carbon nanotubes (MWNTs) are based on the catalytic decomposition of hydrocarbons or CO disproportionation over supported transition metals [1-2]. The materials prepared by these methods are a mixture of MWNTs on the catalytic support together with disordered carbon or carbon shells. Therefore, a purification method is required in order to eliminate all the by-products. The processes which have been reported usually comprise different steps, combining oxidation under various atmospheres at high temperatures and in the liquid phase [1,3-4]. These methods are in some cases not enough effective although very aggressive, damaging the nanotubes walls [1]. Moreover, opening of MWNTs is a topics of high interest due to the potential applications of open nanotubes, that requires an additional treatment. In the present work, a single step method for the simultaneous purification and opening of carbon nanotubes is presented.

Experimental

Two types of catalytic MWNTs have been selected: a) nanotubes obtained by decomposition of acetylene over cobalt supported on zeolite NaY (2.5% of metal) (sample NTNaY) [1]; b) prepared by decomposition of acetylene at 600^0C on Co particles from solid state solution (sample A/CoMgO) [2].

The purification and opening reaction is performed by physically mixing NaOH with the MWNTs at NaOH/carbon ratio of 4/1 and heat treating between 600-800°C in a N_2 flow of 250ml/min. After reaction the materials are extensively washed in diluted HCl and water, and characterized by SEM and TEM.

Results and Discussion

The MWNTs prepared by the two methods present some differences. NTNaY present a large amount of metallic particles and amorphous carbon as can be observed in the SEM (Figure 1a) and TEM (Figure 1b) pictures. The TEM picture presented in Figure 1c shows that their tips are mainly closed and surrounded by amorphous carbon. The A/CoMgO MWNTs present only metallic impurities in small amount, and their tips are always closed [2].

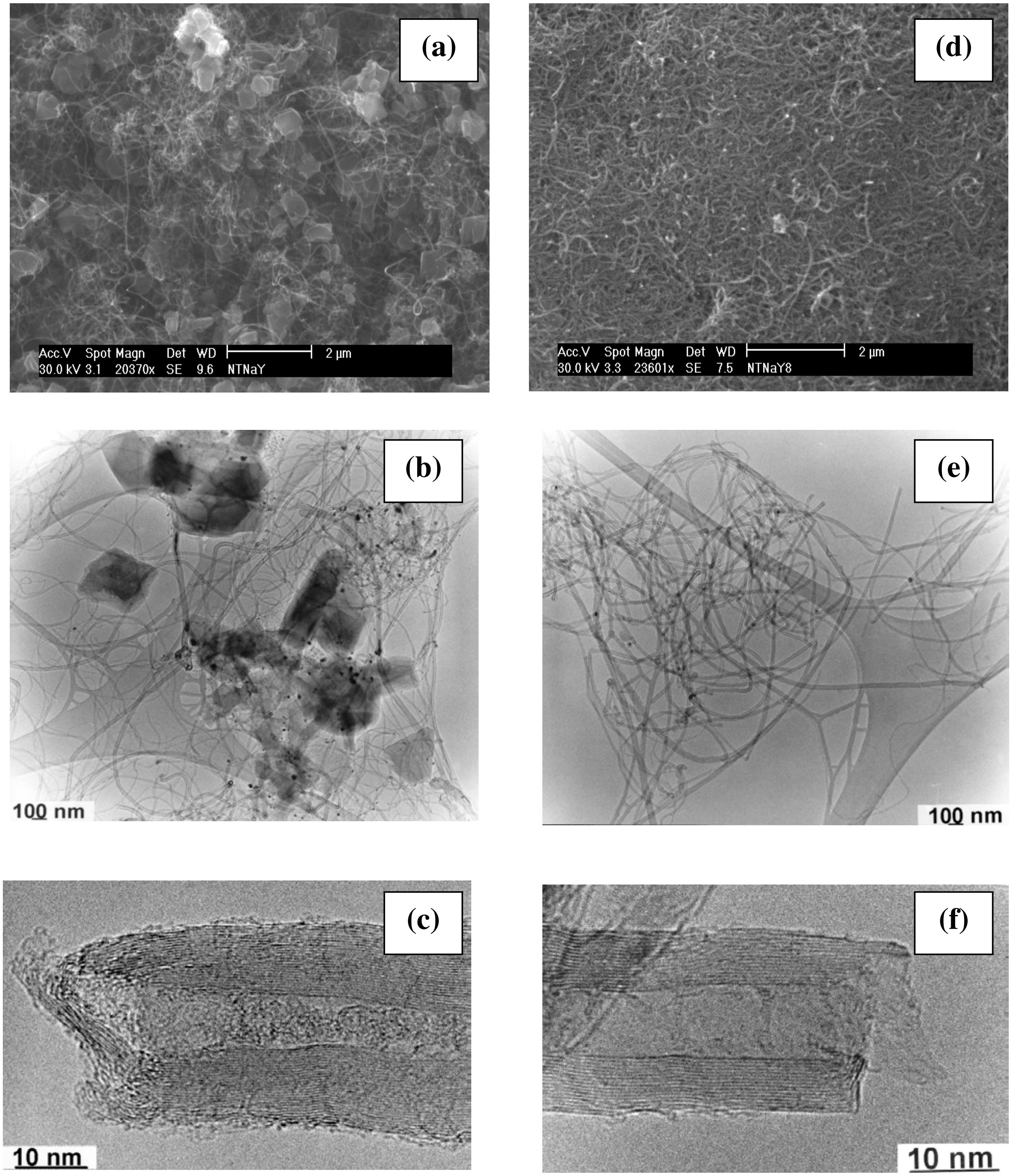

Figure 1. Electron microscopy images on the nanotubes NTNaY .
Pristine MWNTs: a)SEM; b,c)TEM.
MWNTs after NaOH treatment: d)SEM; e,f)TEM

As an example, the SEM (Figure 1d) and TEM (Figure 1e) pictures illustrate the effect of a NaOH treatment at 800°C during 1 hour on the sample NTNaY, which initially contained high amounts of impurities. After the NaOH treatment, it is easy to observe that only nanotubes are remaining. In addition, the TEM observations (Figure 1f) show that during the purification process all the nanotubes tips were opened. From Figure 1f, it is also observable that the nanotube walls are not damaged.

The conditions of the reaction ie. temperature or time, depend on the nature of the pristine material. Thus, for MWNTs with a low amount of impurities and closed tips as the A/CoMgO, a mild treatment ca. 600°C during 1 hour was shown to be enough to open all the nanotube tips. In addition, the method presented here was even effective to open the tips of MWNTs annealed at high temperatures.

The process developed for the purification and opening of MWNTs is based on the particularities of the solid reaction between NaOH and carbon materials. Indeed, it was found that the reactivity of NaOH depends on the structural/microtextural organization of the carbon material [5]. The reaction between carbon materials and alkaline bases as NaOH and KOH starts with redox reactions which produce the metal carbonate (Na_2CO_3 or K_2CO_3) and metallic Na or K. The K metal produced from these redox reactions with carbon can be intercalated between the graphene layers favoring the generation of defects and pores even in materials with a good structural organization as MWNTs [6]. However, it is well known [7] that metallic sodium cannot be intercalated to a large extent into well organized materials and the reaction between carbon and NaOH can only proceed through the high reactive sites of the material. As a result, NaOH reacts only with the disordered carbonaceous impurities and with the defected parts of the carbon nanotubes, i.e. essentially the tips, while the continuous graphitic layers of the nanotubes walls are not damaged.

Conclusions

In the present work, on the base of the particularities of the NaOH-carbon reaction, a method for the simultaneous purification and opening of MWNTs was developed. High purity open nanotubes could be obtained by using this very simple one step process. The carbon nanotubes are not damaged due to the high selectivity of the reaction.

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