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Journal of Alloys and Compounds 434–435 (2007) 854–857

Journal of ALLOYS AND COMPOUNDS

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# Structural properties of some transition metal highly doped carbon aerogels

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## Abstract

Structural characterization of transition metal highly doped carbon aerogels obtained through the sol–gel polymerization process of the formaldehyde with the potassium salt of 2,4-dihydroxybenzoic acid, followed by metal ions exchange using Ni(II) and Cu(II) aqueous solutions, supercritical drying with liquid $CO_2$ and carbonization at 1050 °C under inert atmosphere has been performed. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy were used and it was found that the metal-containing phase is more homogeneously distributed in Cu-doped carbon aerogels. The presence of the metal species determines both the growth of graphitic nanoribbons and the change of framework of the interconnected carbon particles.

*Keywords:* Carbon aerogels; Sol–gel synthesis; TEM; X-ray diffraction; Raman spectroscopy

## 1. Introduction

Carbon aerogels are a new class of nanoporous materials with controllable and interesting structural properties such as low mass densities, high surface areas, continuous porosities [1–3] and moreover, they offer the possibility to incorporate metallic species in the carbon framework [4]. In the last decade many efforts have been devoted to increase the graphitization of carbon aerogels in order to enhance their electrical conductivity. It was reported [5,6] that transition metals incorporated into the carbon aerogels structure seem to be the best catalysts for graphitization of carbon aerogels.

Recently, carbon aerogels doped with Ni and Cu have been prepared by sol–gel polymerization of formaldehyde with potassium salt of 2,4-dihydroxybenzoic acid followed by an ion-exchange process between $K^+$ doped gel and Ni(II), Cu(II) ion aqueous solutions [7,8]. The resulted metal-doped gels have been dried in supercritical conditions with liquid $CO_2$ and then pyrolyzed in high temperature and inert atmosphere resulting in a monolithic metal-doped carbon aerogel (Me-DCA).

In the present study, our interest was focused on finding the structural properties of the obtained Ni and Cu highly doped carbon aerogels by applying complementary investigation methods like transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. The structural analysis regarding the crystalline nature of graphitic and metallic state of Ni and Cu doped aerogels was performed in comparison with the data obtained for the K-doped carbon aerogel, which is considered throughout of this study as the blank carbon aerogel sample.

## 2. Experimental

### 2.1. Sample preparation

The metal-doped aerogels were prepared by $K_2CO_3$ addition to a 2,4-dihydroxybenzoic acid demineralised water suspension (acid/$K_2CO_3$ molar ratio was 0.5 and acid/water, 0.03 g/cm$^3$), under vigorous stirring. After 30 min, when all the acid is neutralised, the solution becomes clear and after another 30 min, 37% formaldehyde (F) and then $K_2CO_3$ as catalyst (acid/formaldehyde and acid/catalyst molar ratios was 2 and 100, respectively) were added to the solution. The resulting solution was placed into tightly closed glass moulds (7 cm-length × 1 cm-internal diameter) and cured for 1 day at room temperature

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doi:10.1016/j.jallcom.2006.08.100

Table 1
Microstructure parameters of the obtained metal-doped carbon aerogels

| Sample | $D_{\text{eff}}$ (nm) (±0.1) | $<\varepsilon^2>^{1/2}{}_{hkl}$ ($\times 10^{-2}$) (±0.01) | $C_{\text{Me}}$ (%) (±0.05) | Band width | | $R = I_D/I_G$ | $L_a$ (nm) |
|---|---|---|---|---|---|---|---|
| | | | | $\Gamma_D$ (cm$^{-1}$) | $\Gamma_G$ (cm$^{-1}$) | | |
| K-DCA | – | – | 8.7 | 237 | 1.038 | 1.038 | 4.23 |
| Ni-DCA | 76 | 0.15 | 18.9 | 211 | 1.020 | 1.020 | 4.31 |
| Cu-DCA | 61 | 0.23 | 20.8 | 205 | 0.925 | 0.925 | 4.75 |

and 4 days at 70 °C. The resulting $K^+$-doped gel rods were cut into 0.5–1 cm pellets and washed with fresh acetone for 1 day. The $K^+$-loaded gels were then soaked for 3 days in a 0.1 M aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2$, in both cases, renewing every day the metal solutions. The metal-doped gels were washed again with fresh acetone and then dried at $CO_2$ supercritical conditions resulting in metal-doped organic aerogels. They were pyrolyzed at 1050 °C for 3 h under $N_2$ atmosphere, obtaining the metal-doped carbon aerogel (Me-DCA). A K-doped carbon aerogel was also prepared to be used as a blank sample.

### 2.2. *Morpho-structural characterization*

The metal content from the carbon aerogels was determined by elemental analysis performed on an inductively coupled plasma-mass spectroscope (ICP-MS) and the values are presented in Table 1.

Transmission electron microscopy (TEM) observations of the metal-doped carbon aerogels were performed with a Hitachi H-7000 microscope operating at 125 keV.

The X-ray diffraction patterns were recorded in a $\theta$–$2\theta$ Bragg–Bretano geometry with a Siemens D5000 powder diffractometer with Cu Kα incident radiation ($\lambda = 1.5406$ Å) and a graphite monochromator. The microstructure information was obtained by a single X-ray profile Warren–Averbach Fourier analysis, with a method developed by Aldea and Indrea using a XRLINE computer program [9–11].

The Raman measurements of the carbon aerogel samples were performed on a Dilor Labram system equipped with a Leica PL FLUOTAR 100×/0.75 microscope objective, an 1800 lines/mm grating and an external laser with an emission wavelength of 532 nm. In order to ensure that the surface did not degrade a power of 10 mW incident on the sample was employed in the recording of the micro-Raman spectra. The spectral resolution used for all measurements was of about 2 cm$^{-1}$.

## 3. Results and discussion

By inspecting the TEM bright-field images of the metal-doped carbon aerogels presented in Fig. 1 one can observe dispersed metal particles only in the Cu-doped carbon aerogel. The sizes of the particles range from tens to hundreds nanometers in diameter. For the Ni-DCA samples, the Ni nanoparticles could not be sharply visualized by TEM because of their large magnetization (Fig. 1, Ni-DCA). The dark zones observed in the TEM image correspond to agglomerates of nanoparticles. However, additional information can be extracted from the XRD analysis. The diffraction patterns of the investigated samples are presented in Fig. 2.

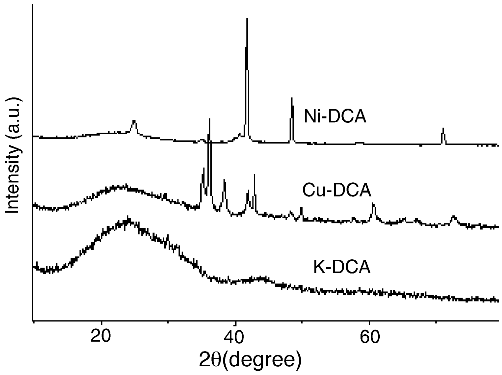

Fig. 2. XRD patterns of metal-doped carbon aerogels.

As can be seen in Fig. 2, the presence of metal/metal oxide phases is evidenced by the appearance of sharp Bragg peaks in the XRD patterns of the investigated Me-DCA. The relative content of crystalline phases and their corresponding crystallite sizes have been determined by Rietveld refinement analysis of those patterns. In order to determine the micro structural parameters of the metal clusters, the (1 1 1) and (2 0 0) metal peaks from the X-ray diffraction profiles were analyzed. The X-ray diffraction line broadening is caused by the small size of the crystallites, the lattice strains, lattice faults, and the experimental diffraction geometry [9]. Effective crystallite mean size ($D_{\text{eff}}$) of the metal nanoparticles together with the root mean square of the micros-

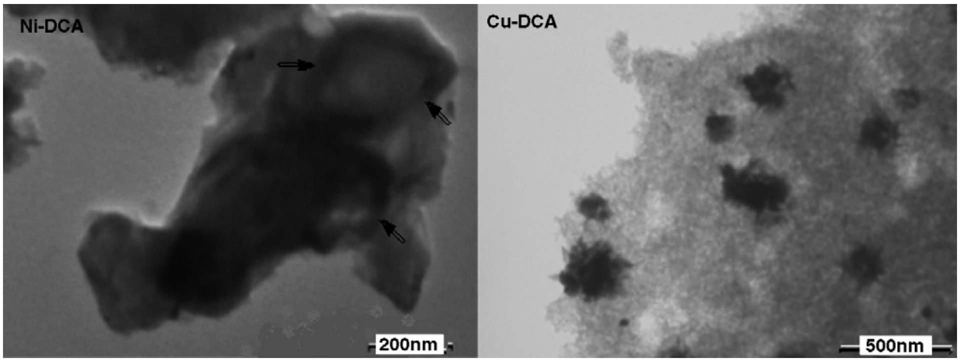

Fig. 1. TEM images of Ni- and Cu-doped carbon aerogels.

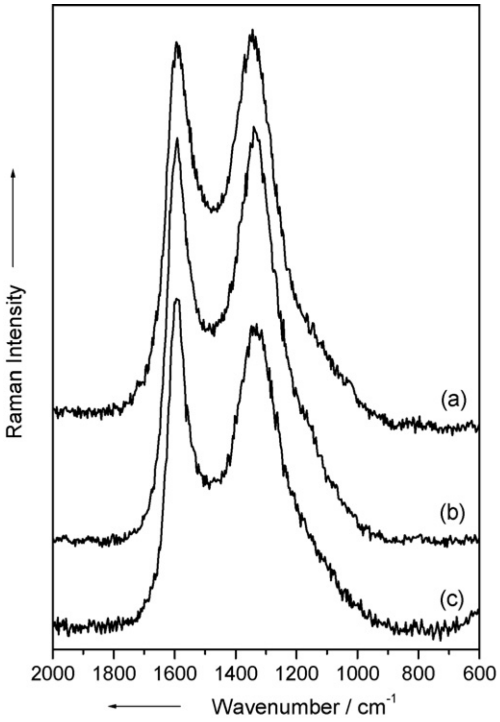

Fig. 3. Micro-Raman spectra of metal containing carbon aerogels: (a) K-DCA, (b) Ni-DCA and (c) Cu-DCA.

trains averaged along [*h k l*] direction ($<\varepsilon^2>^{1/2}{}_{hkl}$) are collected in Table 1.

In both metal-doped carbon aerogel samples a mixture of metal and metal oxides is observed. By comparing the crystallite sizes presented in Table 1 and taking into account that the metal/metal oxides ratio can be correlated with the electronegativity of the doping element one can assume that the metallic nanoparticles tend to form agglomerates, as in the TEM images.

Complementary information concerning the graphitization process induced by the metal presence was obtained by using Raman spectroscopy. By looking at the Raman spectra of the as-prepared carbon aerogels (Fig. 3) one can see two distinct peaks, one associated with the $2E_{2g}$ mode near 1580 cm$^{-1}$ (G-band) that is always present in all carbon and graphite materials and the other one, near 1360 cm$^{-1}$ (D-band), attributed to the $A_{1g}$ mode and associated with the in-plane disorder [5,12]. This latter band originates from the disorder-induced scattering produced by imperfections or loss of hexagonal symmetry in the carbon structure. Since this Raman band does not appear in perfect graphite crystals, it has been frequently used to evaluate the degree of imperfection or crystallinity of graphite.

The most important parameters obtained from the Raman spectra of the metal containing carbon aerogels, i.e. the half-width and the intensity ratio of the D- to G-band ($R = I_D/I_G$), are listed in Table 1. One can observe that the presence of Ni and especially Cu lead to a slight narrowing of both D- and G-bands and to a decrease of the *R*-values. In a previous study [5], in which the graphitization of carbon aerogels by transition metals was studied by means of Raman spectroscopy, the increase of the *R*-values was associated with carbon aerogel particles shrinkage, which induces the loss of microporosity and imperfections in the carbon structure, enhancing in this way the D-band intensity. One should mention that the metal amounts found in the carbon aerogels under investigation in the present study are considerably higher than those reported in the above-mentioned reference. By inspecting the *R*-values obtained from the blank and metal-doped carbon aerogels (see Table 1) one can remark the validity of this hypothesis. Thus, we can conclude that even for such high metal contents, the decrease of the intensity ratio values, *R*, occurs as a result of the stacking of the graphitic layers by the catalytic effect of the metals and by the smaller shrinkage of the microporosity of these samples. The more pronounced graphtization process evidenced for the Cu doped aerogel is most probably due to the existence of the dispersed metallic nanoparticles into the carbon framework revealed by the TEM images. The in-plane widths of the graphene layers ($L_a$), have been further obtained by using their linear dependency with respect to the inverse of the relative integrated intensity ratio $R$, $L_a$ (nm) = 4.4/$R$, and are presented in Table 1. However, it is worthy mentioning that these values have to be considered with certain caution because the above equation is valid only as a first approximation to $L_a$ when considering materials with a certain degree of disorder.

## 4. Conclusions

Structural investigations of the Ni and Cu highly doped carbon aerogels have been performed by using complementary TEM, XRD and Raman spectroscopy. The structural properties of the metal-doped carbon aerogels depend on the nature of doping metal. TEM and XRD measurements evidenced the existence of dispersed Cu nanoparticles and the trend for both Cu and Ni particles to form agglomerates. Furthermore, from the XRD data and the analysis of the Raman spectra, information concerning the effective crystallite mean size of the metal nanoparticles and regarding the graphitization process of the carbon aerogel structure have been obtained.

Further investigations are in progress in order to test the catalytic, electrical and magnetic (for Ni-DCA) properties of the as-prepared transition metal-doped carbon aerogels.

## Acknowledgments

Part of this work was carried out during the 1-year stay of C. Cotet at the ICMAB-CSIC in Spain under the EU Marie Curie Training Site Grant No. HPMT-CT-2000-0006. Dr. A. Roig is kindly acknowledged for the tutoring during such period and for critical reading of this manuscript.

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