Tailored production of nanostructured metal-doped carbon foam by laser ablation of selected organometallic precursors

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ABSTRACT

The present work pretends to illustrate the potential of using selected organometallic precursors for the tailored laser ablation synthesis of metal-doped carbon foams. These materials consist of metal nanoparticles embedded within nanostructured carbon matrices. The composition, metal-doping, and structure of these metal/carbon nanocomposites can be tailored by suitably choosing the metals and ligands of the irradiated organometallic targets. The results reported here indicate that precursors containing triphenylphosphine ligands tend to yield larger amounts of ablation products where graphitic structures are observed in appreciably larger quantities than the employed non-aromatic targets. It is also demonstrated here that the employed metals do not promote the growth of the observed graphitic nanostructures. The convenient laser ablation technique **here presented**, based on the use of molecular precursors, would enable the facile production of multifunctional nanostructured carbon materials with a range of tunable properties.

1. Introduction

Nanostructured carbon materials are attracting continuing attention because their unique structural and physical properties, combined with their high surface area and low mass densities, can be utilized in the development of novel electrodes for double-layer capacitors and rechargeable batteries, adsorbents, thermal insulators, and a whole plethora of other applications [1-8]. Moreover, metal-doping can provide additional

functionalities to these materials, allowing them to be efficiently employed in fuel cells and other electrochemical devices, catalysis, and sensors [4,9-11]. Several metal-doping strategies are currently being applied to nanostructured carbon materials. Thus, metal-doped carbon aerogels are commonly prepared by different metal deposition methods (including metal sublimation and metal impregnation under supercritical CO₂ conditions), by ion-exchange, or by addition of metal precursors to the starting monomers (typically resorcinol and formaldehyde mixtures) [4,12-15]. On the other hand, chemical [9,16], electrochemical [17], and physical [10] methods are commonly employed for the metal decoration of carbon nanotubes (CNTs).

Much effort is being devoted to the design of synthetic routes for controlling the structure and properties of nanostructured carbon materials using molecular precursors. Thus, graphitic nanotubes exhibiting long-range molecular ordering and tunable properties are produced by self-assembly of a hexa-*peri*-hexabenzocoronene derivative, which acts as a molecular building block [18]. On the other hand, Baughman *et al.* have proposed an elegant topochemical route based on the polymerization of cyclic diacetylene oligomers for the production of CNTs of well-defined chiralities [19]. When it comes to nanostructured **extended solids** such as carbon aerogels, a remarkable control on their structure, porosity, and transport properties can be achieved by conveniently adjusting the sol-gel polymerization conditions (the molar ratio of the employed monomers, and subsequent curing and drying processes of the resulting hydrogels) and further thermal- and carbonization processes, and by metal-doping [14,20]. **The** one-step production of nanostructured Au-doped carbon foam by laser ablation of a triphenylphosphine-containing organometallic Au salt (bis(acetylacetonate)aurate(I) of bis(triphenylphosphine)iminium, PPN[Au(acac)₂]) was reported **previously** [21]. This carbon foam material consists of nanostructured carbon

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matrices containing both graphitic and amorphous carbon, and comprising fcc crystalline Au nanoparticles, 3 to 7 nm in diameter. The present work pretends to illustrate the potential of using selected organometallic precursors for the controlled synthesis of metal-doped nanostructured carbon foam. It is here demonstrated that the morphology and composition of these nanostructured carbon foams can be tailored by conveniently choosing the ligands and metals of the molecular precursors ablated, which is certainly interesting towards the development of potential applications for these novel nanostructured carbon materials. Moreover, it is shown here that nanostructured carbon foam can also be efficiently produced by laser ablation of triphenylphosphine, the pure aromatic ligand employed.

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2. Experimental

Several aromatic and non-aromatic organometallic targets have been investigated in order to assess the effect of the employed metals and ligands on the structure of the resulting metal-carbon nanocomposites. Thus, laser irradiation of triphenylphosphine-containing organometallic compounds bis(triphenylphosphine)iminium tetrachloroaurate(III) (PPN[AuCl₄]), chloro(triphenylphosphine)gold(I) (AuClPPh₃), and chlorotris(triphenylphosphine)copper(I) (CuCl(PPh₃)₃) has been performed. The syntheses of these organometallic compounds have been reported elsewhere [22-24]. Alternatively, non-aromatic 1,3,5-triaza-7-phosphaadamantane gold(I) chloride (AuCIPTA [25]) and commercial (Sigma-Aldrich) copper(II)acetylacetonate (Cu(acac)₂) organometallic compounds were also ablated. A few square centimeter layers of these precursors in powder form were placed on top of ceramic tile substrates

and then irradiated in air at atmospheric pressure inside an evaporation chamber with a continuous wave Baasel Lasertech Nd:YAG laser ($\lambda = 1.064$ microns, 57 W) at a scan rate of 100 mm/s (spot size: ~60 microns). The produced soot was collected in an entangled metal wire placed on top of the ablated precursors.

The structure of the synthesized materials ~~were~~was characterized by scanning electron microscopy (SEM, Hitachi S-3400N and LEO 1590 VP microscopes), and transmission electron microscopy (TEM, JEOL JEM-3000F microscope equipped with an Oxford Instruments ISIS 300 X-ray microanalysis system and a LINK “Pentafet” detector for energy dispersive X-ray spectroscopy (EDS) analyses). Further characterization studies included micro-Raman spectroscopy (Dilor XY Raman spectrometer, $\lambda_{exc}=514.5$ nm), X-ray diffraction (XRD, CuK_{α} radiation, Bruker D8 Advance Series 2), and thermogravimetric analysis (TGA, SETARAM Setsys Evolution, samples were analyzed in Pt pans at a heating rate of 10°C/min up to 850°C in an atmosphere of air flowing at 100 mL/min).

3. Results and discussion

The laser irradiation of the employed PPh_3 -containing organometallic precursors resulted in milligram quantities of soot exhibiting a fibrous appearance. SEM characterization showed that the microstructure of this material exhibited the foam-like texture (Fig. 1a) which results ~~of~~from the aggregation of “necklace”-like ensembles of nanobeads (Fig. 1b), similar to that observed in other “spongy” carbon materials [5-7,20,21,26-28].

Transmission electron microscopy (TEM) studies revealed that the foam-like soots produced by laser ablation of PPN[AuCl₄] and AuClPPh₃ are, in fact, three-component materials (Fig. 2) consisting of A) crystalline fcc Au nanoparticles (Fig. 3, area A shows the fcc structure along the [01 $\bar{1}$] zone axis of the Au nanoparticles; the corresponding FFT is shown in Fig. 3b), 5-30 nm in diameter (typically larger than 20 nm in carbon foams produced by laser ablation of AuClPPh₃) embedded within amorphous carbon nanoparticles, B) amorphous carbon aggregates (30-60 nm in diameter), and C) carbon aggregates containing multilayered graphitic nanostructures. While similar structures have been already reported for Au-doped carbon foams [21], the TEM characterization studies presented here reveal for the first time that **they** can be eventually observed as independent, separate components in the produced soots. On the other hand, the Au nanoparticles usually ~~show exhibit~~ twinning, a common feature in metal nanoparticles [29-31], as can be observed in area B of Fig. 3a, and confirmed by the corresponding FFT, which indicates diffuse streaking along [111] (Fig. 3c).

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XRD patterns of these Au-doped carbon foams displayed the characteristic peaks for fcc crystalline Au. Average Au crystallite size of ~14 nm and 23 nm were calculated from the Au diffraction peaks width measured in the XRD patterns of the foams synthesized from PPN[AuCl₄] and AuClPPh₃ precursors, respectively, using the Scherrer equation [32]. These values are significantly larger than those calculated for foams ~~that result derived of from~~ the laser ablation of PPN[Au(acac)₂] (~5 nm) [21]. These results therefore suggest that the metal crystallite size in these metal-doped carbon foams can be tuned by suitably choosing the composition and size of the employed ligands.

Although the presence of transition metal nanoparticles is required in the formation of graphitic nanostructures in thermally-annealed metal-doped carbon aerogels

[4,12,33,34], no obvious link between the Au nanoparticles and the synthesized graphitic structures has been observed here, however. This issue also occurs in the Cu-doped carbon foams produced by laser ablation of $\text{CuCl(PPh}_3)_3$. TEM characterization indicates that these foams are also multi-component materials which consist of crystalline fcc Cu nanoparticles (Fig. 4a, in agreement with the measured periodicities and the corresponding Fast Fourier Transform (FFT) analysis shown at the inset), typically 10 to 30 nm in diameter, diluted within amorphous carbon aggregates, amorphous carbon nanoparticles that eventually coalesce into large aggregates (Fig. 4b), also exhibiting a broad diameter distribution (typically, around 50 nm in diameter), and graphitic nanostructures (Fig. 4c). TEM micrographs do not either show here a clear involvement of the Cu nanoparticles in the growth of these graphitic structures. Interestingly enough, P was only detected in energy dispersive X-ray spectroscopy (EDS) analyses performed on the amorphous carbon aggregates and the metal-containing aggregates, but not within the observed graphitic stackings of these Cu- and Au-doped carbon foams.

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The results reported here indicate that the metal-doping of these nanocomposite foams can be tailored by conveniently choosing the metals of the irradiated molecular precursors. Moreover, the chemical composition of the employed ligands also plays a major role in the composition and structure of the produced soots and the nature of the carbon matrices produced by ablation. Thus, laser ablation of Cu(acac)_2 results in the production of a powder-like soot, that eventually also exhibits some fibrillar texture, but in significantly lower amounts than when employing PPh_3 -containing targets. SEM characterization revealed that the produced soot consisted of assemblies of ribbon-like nanostructures (Fig. 1c,d). TEM studies indicated that the synthesized soot consisted of Cu nanoparticles of typically 20 to 40 nm in diameter embedded within interconnected

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amorphous carbon aggregates (Fig. 5a). High resolution TEM images and FFT analyses show fcc crystalline Cu features (Fig. 5b). Some degree of carbon organization can eventually be observed in these carbon matrices in the form of nanometer-long graphene-like structures (Fig. 5c), similar to those observed in nanostructured carbon materials produced by pyrolysis of benzene or ethanol [35]. In this case, however, the recombination processes that occur in the plasma plume did not lead to the formation of multilayered graphitic structures. On the other hand, no soot was produced by laser irradiation of AuClPTA.

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These results are clearly an indication that the employed ligands behave differently during these laser ablation experiments. It is also worth mentioning that TEM characterization studies reveal that the irradiation of PPh₃-containing organometallic compounds led to the production of soot with higher metal nanoparticle dilution within the carbon matrices than Cu(acac)₂ (Figs. 4,5), therefore indicating that the PPh₃ ligand acts as more efficient carbon feedstock than the acetylacetonate ligand. This point has been further confirmed by TGA analyses: thus, while air oxidation up to 850°C of the metal-doped carbon foams produced by laser ablation of CuCl(PPh₃)₃, PPN[AuCl₄], and AuClPPh₃ left ca. 16, 11, and 33 wt.% residues, respectively, the Cu content is as high as ~90 wt. % in the materials synthesized by irradiation of Cu(acac)₂.

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The Raman spectra of the produced nanostructured carbon foams (Fig. 6) show two broad bands centered at ~1355 cm⁻¹ (D-band) and ~1588 cm⁻¹ (G-band) of equivalent intensities. This feature is typical of short-range ordered sp²-bonded carbon [36], including defective graphites [37,38], and other nanostructured carbon materials such as carbon nanofoam [6] and carbon aerogels [26,34]. According to the evolution of the Raman spectrum for progressive amorphization [36], the band positions and their relative intensities would place these materials in a stage intermediate between

nanocrystalline graphite and sp^2 -bonded amorphous carbon, in the limit of validity of the Tuinstra and Koenig expression [39]. The latter relates the I_D/I_G ratio to the in-plane size of the graphitic nanocrystalline regions (L):

$$L(\text{nm}) = 4.4(I_D/I_G)^{-1}$$

In order to apply this expression we have decomposed the Raman spectra as a superposition of bands (Fig. 6). Asymmetric profiles are needed for the D and G bands, which are attributed to the short correlation lengths of the ordered regions. L values of ≈ 3.6 nm and ≈ 1.8 nm for the $\text{CuCl(PPh}_3)_3$ and Cu(acac)_2 products, respectively, were thus obtained. Though these figures are subject to large errors due to the low intensity of the spectra and the difficulties in subtracting a background, it is clear that the higher intensity ratio of the D- to G bands measured on the Raman spectra corresponding to the nanostructured carbon material produced using the Cu(acac)_2 precursor (Fig. 6b) is indicative of the higher degree of carbon disorder of this material, which is in good agreement with the TEM results described above. This higher degree of carbon disorder, together with the low carbon content of this material account for the lower signal-to-noise ratios measured in their Raman spectra (Fig. 6b).

The laser ablation of triphenylphosphine (PPh_3), the employed aromatic ligand, was then performed in order to further clarify the role of metals in the formation of the observed graphitic structures in nanocomposite carbon foams. Nanostructured carbon foams were readily produced by laser ablation of PPh_3 . SEM micrographs of these materials (Fig. 7a) are similar to those corresponding to soot produced by laser irradiation of PPh_3 -containing organometallic compounds (Fig. 1a,b). TEM investigations indicate that these foams consist of amorphous carbon aggregates, 30-40 nm in diameter (Fig. 7b) and multi-layered graphitic nano-ribbons (Fig. 7c), that can be

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clearly observed as separate components of these materials, as shown in the insets depicted in Fig. 7b,c. These results therefore further confirm that the metal of the employed organometallic compound does not apparently play an essential role in the formation of the observed graphitic structures. It is however expected that the use of other transition metals would lead to the formation of different carbon nanostructures, as it has been reported for similar plasma assisted processes [40,41]. Again, EDS analyses confirmed the absence of P in the graphitic carbon aggregates. Raman spectra (Fig. 8) are again typical of short-range ordered sp^2 carbons; the measured in-plane graphitic crystallite size derived from application of the Tuinstra and Koenig equation [39] is ≈ 3 nm. This small in-plane graphitic crystallite size value together with the presence of significant amounts of amorphous carbon in these materials led to the absence of graphitic features in XRD diffractograms.

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The fact that the carbon foams here described were synthesized in air at atmospheric pressure leads us to conclude that these nanostructured materials are produced within the generated plasma plume as a result of the assembly of high-temperature, ionized clusters [21], and not as a consequence of conventional combustion. The starting molecular precursors may thus undergo transformation not via conventional pyrolysis or combustion, but rather through an alternative photo-induced mechanism [42]. The latter has its origin in the intense plasma plume observed, possibly attained via combination of moderate irradiance levels (ca. 10 kW cm^{-2}) with the energy released by the exothermic transformation of the precursors, triggered by the laser irradiation itself. This is the subject of current research.

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The presence of amorphous carbon and graphitic structures together but as separate components in the carbon matrices may suggest that the formation of the latter might be the result of incomplete, high temperature carbon restructuring of the amorphous carbon

aggregates [35], which would therefore also lead to P removal. The results described here would rather indicate that the presence of conjugated moieties and clusters in the ablated materials and in the plasma plume might play a key role in the formation of crystalline carbon nanostructures, as it occurs in the production of multi-walled carbon nanotubes (MWNTs) and carbon nanohorns by arc-discharge- and laser-assisted evaporation of graphite [43,44], and in the synthesis of shell-shaped graphitic nanostructures by laser irradiation of acetylene [45].

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4. Conclusions

Nanostructured carbon foam can be ~~conveniently~~^{easily} produced in a single step by laser irradiation of organometallic compounds and PPh₃. The here reported ability to control the composition, metal-doping, and structure of the synthesized materials, as well as the dilution of the metal nanoparticles within carbon matrices and the metal nanoparticle- and crystallite size by conveniently choosing the ligands and metals of the irradiated molecular precursors might be usefully employed in tuning the physical properties of metal/carbon nanocomposites, and offers fascinating opportunities for the production of novel metal/carbon nanocomposites, metal-doped nanocarbons, and nanostructured foam-like materials. Further control of the metal nanoparticle size, the relative amounts of amorphous carbon and graphitic nanostructures, and the material overall structure might be achieved by suitably adjusting the employed laser parameters and atmosphere composition and pressure (that affect both the photon-molecular precursor interaction and the confinement of the highly reactive, high temperature, ionized species within the generated plasma plume) [46,47], as well as by additional carbon foam processing.

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Future work will focus on investigating the porosity and physical properties of these promising metal-doped nanostructured carbon materials, as well as in evaluating their potential applications in catalysis and as components for sensor- and electrochemical devices.

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Figure Captions

Fig. 1 - SEM characterization of nanostructured carbon materials produced by laser ablation of $\text{CuCl}(\text{PPh}_3)_3$ (a,b), and $\text{Cu}(\text{acac})_2$ (c,d). These materials are the result of “rosary”-like assemblies of particles (b) and ensembles of “ribbon”-like structures (d).

Fig. 2 – TEM characterization of Au-doped carbon foams produced by laser ablation of $\text{PPN}[\text{AuCl}_4]$, showing that the synthesized materials are three-component nanocomposites consisting of (A) fcc Au nanoparticles embedded within amorphous carbon (the insets display a high-resolution TEM image of a Au nanoparticle and its corresponding FFT), (B) amorphous carbon aggregates, and (C) multilayered graphitic nanostructures.

Fig. 3 - (a) High resolution TEM image of a Au nanoparticle produced by laser ablation of AuClPPH_3 where areas marked as A and B indicate the presence of twinning, (b) FFT of area A, and (c) FFT of area B.

Fig. 4 - TEM micrographs of the three components found in the Cu-doped carbon foams produced by laser ablation of $\text{CuCl}(\text{PPh}_3)_3$: (a) fcc Cu nanoparticles embedded within amorphous carbon (the corresponding FFT of the displayed fcc Cu nanoparticle is shown in the inset), (b) amorphous carbon aggregates, and (c) graphitic nanostructures.

Fig. 5 - TEM micrographs of the nanostructured carbon material produced by laser ablation of $\text{Cu}(\text{acac})_2$. (a) Low magnification image showing Cu nanoparticles embedded in the carbon matrix, (b) higher magnification image and corresponding FFT of fcc Cu nanoparticles embedded within amorphous carbon aggregates, and (c) micrograph of the amorphous carbon matrix evidencing nanometer-long graphene-like structures.

Fig. 6 - Raman spectra of the nanostructured carbon materials produced by laser ablation of $\text{CuCl}(\text{PPh}_3)_3$ (a) and $\text{Cu}(\text{acac})_2$ (b).

Fig. 7 - Electron microscopy characterization of nanostructured carbon foam produced by laser ablation of PPh_3 . (a) SEM micrograph showing the spongy texture of the produced material, and high resolution TEM images of amorphous carbon aggregates (b, TEM micrograph of ensembles of amorphous carbon particles is shown in the inset), and graphitic nanostructures (c, low resolution TEM micrograph of aggregates containing graphitic nanostructures is shown in the inset).

Fig. 8 - Raman spectrum of the nanostructured carbon foam produced by laser ablation of PPh_3 .

Fig. 1 - SEM characterization of nanostructured carbon materials produced by laser ablation of $\text{CuCl(PPh}_3)_3$ (a,b), and Cu(acac)_2 (c,d). These materials are the result of “rosary”-like assemblies of particles (b) and ensembles of “ribbon”-like structures (d).

Fig. 2 – TEM characterization of Au-doped carbon foams produced by laser ablation of PPN[AuCl₄], showing that the synthesized materials are three-component nanocomposites consisting of (A) fcc Au nanoparticles embedded within amorphous carbon (the insets display a high-resolution TEM image of a Au nanoparticle and its corresponding FFT), (B) amorphous carbon aggregates, and (C) multilayered graphitic nanostructures.

Fig. 3 - (a) High resolution TEM image of a Au nanoparticle produced by laser ablation of AuClIPPh_3 where areas marked as A and B indicate the presence of twinning, (b) FFT of area A, and (c) FFT of area B.

Fig. 4 - TEM micrographs of the three components found in the Cu-doped carbon foams produced by laser ablation of $\text{CuCl}(\text{PPh}_3)_3$: (a) fcc Cu nanoparticles embedded within amorphous carbon (the corresponding FFT of the displayed fcc Cu nanoparticle is shown in the inset), (b) amorphous carbon aggregates, and (c) graphitic nanostructures.

Fig. 5 - TEM micrographs of the nanostructured carbon material produced by laser ablation of $\text{Cu}(\text{acac})_2$. (a) Low magnification image showing Cu nanoparticles embedded in the carbon matrix, (b) higher magnification image and corresponding FFT of fcc Cu nanoparticles embedded within amorphous carbon aggregates, and (c) micrograph of the amorphous carbon matrix evidencing nanometer-long graphene-like structures.

Fig. 6 - Raman spectra of the nanostructured carbon materials produced by laser ablation of $\text{CuCl(PPh}_3)_3$ (a) and Cu(acac)_2 (b).

Fig. 7 - Electron microscopy characterization of nanostructured carbon foam produced by laser ablation of PPh_3 . (a) SEM micrograph showing the spongy texture of the produced material, and high resolution TEM images of amorphous carbon aggregates (b, TEM micrograph of ensembles of amorphous carbon particles is shown in the inset), and graphitic nanostructures (c, low resolution TEM micrograph of aggregates containing graphitic nanostructures is shown in the inset).

Fig. 8 - Raman spectrum of the nanostructured carbon foam produced by laser ablation of PPh₃.