Surface decoration of carbon nanosheets with amino-functionalized organosilica nanoparticles

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ABSTRACT

Carbonaceous nanosheets decorated with amino-functionalized organosilica nanoparticles have been synthesized by a direct pyrolysis of betaine at 400 °C in air, followed by a simple surface treatment with ([3-(2-aminoethylamino) propyl]trimethoxysilane under reflux conditions. Both pristine and organosilica modified carbon nanosheets (OMCNs), were characterized by Fourier-transform infrared (FTIR), Raman, and electron paramagnetic resonance (EPR) spectroscopies, transmission electron microscopy and thermal analysis methods. The experimental data reveal a dramatic increase in the number of radical centers on the surface of the developed OMCN hybrid. The organosilica nanoparticles, ranging in size between 3 and 15 nm, are spherical and homogeneously anchored on the surface of carbon nanosheets. The formation of C—O—Si bridges between carbon sheets and the organosilica nanoparticles has been supported by FTIR and EPR. These nanoparticles are bound to the nanosheet surface together with individual functional organosilane groups at a spacing of about 4 Å distance. The final hybrid is the complex nanosystem composed of 2D carbon nanosheets, spherical organosilica nanoparticles and immobilized amino organosilane molecules.

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1. Introduction

Chemical functionalization of carbon nanotubes, fullerenes, mesoporous carbon, graphene and other carbon-based nanostructures represents the crucial step in order to control their properties towards particular applications [1–4]. The considerable part of the modification procedures [2,5] is focused on the development of advanced carbon composites and hybrids analogs [6–10]. Generally, the outer surface of the pristine non-functionalized materials has a graphite-like, polyaromatic character, similar to carbon blacks or carbon fibers. However, from the chemical point of view, their surfaces are not active enough for the above purpose. Therefore, in order to increase the number of surface active sites on these carbon nanostructures, they are usually subjected to various post-treatment procedures including oxidation, polymer coating and grafting [11–14].

In contrast to other carbonaceous materials, ultrathin carbon nanosheets including graphene [15] are usually oxygenated, bearing hydroxyl and epoxide functional groups on their basal sheets and carbonyl and carboxyl groups at their edges. These modified nanosheets define a peculiar class of carbon materials with high surface-to-volume ratio, smooth surface morphologies and thin edges, flexibility and elasticity, high thermal and chemical stability, unique transport properties and finally, lightness. In this respect, carbon nanosheets are promising candidates for hydrogen storage materials, catalyst supports, fillers, templates, and due to their electrical properties these may also be suited for electronic and optoelectronic applications [16–23].

The active carbon nanosheet surfaces portray them also as ideal candidates in fabricating novel nanocomposites or hybrid materials since they can be easily modified by incorporation of various functional groups. The decoration of carbon nanosheets with organosilica nanoparticles defines an important class of synthetic materials in which the physicochemical properties of the carbon structure are uniquely combined with those of the silica constituent, thereby leading to remarkable functionalities that do not exist in either of the initial solids. Multifunctional silica particles are increasingly used for bioanalysis and biomedical applications [24] and their best commercial example is the MQ resins composed of clusters of silicate Q-groups terminated with trimethylsiloxy-M groups or hydroxyl groups [25]. Other applications of these multifunctional particles involve the pressure-sensitive adhesives, components for cosmetics and for the polymer reinforcement [26–28]. Commonly, the preparation of the nanoparticles involves
the modification of external surfaces of silica particles using organosilicates containing thiol or amino groups. Alternatively, these can be fabricated directly from a single-thiol organosilicate precursor by means of a one-pot synthesis [29]. Combining the above two kinds of nanomaterials it is possible to develop new hybrids endowed with synergetic and improved properties. For example, such nanomaterials could be used as selective adsorbents to remove heavy metal ions from water. In polymer science, these hybrids could be intimately mixed with many organic polymers, facilitating synthesis of graphene-polymer composites.

In the present work, our effort has been focused on preparing a new hybrid consisting of carbon nanosheets and organosilica nanoparticles. The hybrids were prepared from ultrathin carbonaceous nanosheets via post-synthesis grafting method using organoalkoxysilanes containing one and two amino groups. The pristine nanosheets have been synthesized by direct pyrolysis of betaine ([CH$_3$]$_3$N=CH$_2$COO$^-$) [30] in air using a simple and inexpensive method which produces bulk quantities of powdered nanosheets in a high yield, thus enabling their large-scale applications. The final hybrid, accessible in a large scale, combines the unique properties of the two-dimensional nanostructures (pristine carbon sheets), nanoparticles (organosilica) and molecular species (amino organosilane).

2. Experimental

2.1. Synthesis of organosilica modified carbon nanosheets (OMCNs)

The pristine carbon nanosheets subjected to the modification process were prepared by pyrolysis of betaine as reported earlier [30]. Typically, 1 g of anhydrous betaine (C$_5$H$_7$N$_2$O$_2$, Sigma–Aldrich) was thermally treated in air at 400 °C for 2 h to obtain a lightweight black-brown powder containing exclusively carbonaceous nanosheets. Grafting procedure to obtain organosilica modified carbon nanosheet (OMCN) hybrid material consists of dispersing 0.084 g of the pristine carbon nanosheets in 30 ml of water under reflux conditions (100 °C) with the desired amount (0.376 g) of 3-[2-aminoethylamino] propyltrimethoxysilane, (AAPTMS; Fluka 06668). The pH value was adjusted to 9–10. The final solution is then kept under reflux conditions for 8.5 h. Finally, the powder was isolated by filtration, washed with ethanol and water and dried at 70 °C.

2.2. Characterization of the OMCN hybrid

Fourier-transform infrared (FTIR) spectra of powdered samples, dispersed in KBr pellets were measured with a PerkinElmer GX, Fourier transform spectrometer in the frequency range of 400–4000 cm$^{-1}$. Raman spectra were recorded with a micro-Raman system RM 1000 Renishaw using a laser excitation line at 532 nm (Nd-YAG) in the range of 500–2000 cm$^{-1}$. Laser power ~10 mW was used with 2 μm focus spot in order to avoid photodecomposition of the samples. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed using a Perkin Elmer Pyris Diamond TG/DTA instrument. Samples of approximately 5 mg were heated in air from 25 °C to 900 °C, at a rate of 5 °C/min. Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2100 transmission electron microscope equipped by LaB$_6$ cathode (accelerating voltage of 200 kV; point-to-point resolution of 0.194 nm). A drop of high-purity distilled water, containing the ultrasonically dispersed particles, was placed onto a holey carbon film supported by a copper-mesh TEM grid and air-dried at room temperature. Electron paramagnetic resonance (EPR) spectra were recorded with a Brucker ER200D spectrometer at liquid-nitrogen temperatures, equipped with an Agilent 5310A frequency counter. The spectrometer was running under homemade software based on LabView [31]. Progressive saturation analysis was performed as reported previously [32]. Spin quantification was performed using DPPH as a spin standard. Numerical simulation of the experimental EPR spectra was performed based on the second order perturbation theory, using the software WinEPR Simfonia v. 1.25 by Bruker Analytische. The surface properties of the hybrid were probed by studying Cu$^{2+}$ binding by EPR spectroscopy. 35 ml of 0.05 M CuCl$_2$ was added to the water solution containing 0.1 g of the OMCN hybrid and stirred for 20 h at room temperature (pH 4.5). Then the sample was washed two times with absolute methanol and deionized water and finally centrifuged. The sample was designated as OMCNs-Cu$^{2+}$.

3. Results and discussion

3.1. Characterization of hybrids

Fig. 1 shows the FTIR spectra of pristine material, of hybrid OMCNs and the spectrum of AAPTMS for comparison. The spectrum of the unmodified nanosheets is very similar to that of graphite oxide showing two strong bands at 1720 cm$^{-1}$ and 1618 cm$^{-1}$ and a very broad band of medium intensity at absorption range of 900–1500 cm$^{-1}$. According to previous studies, the bands at 1720 cm$^{-1}$ and 1618 cm$^{-1}$ can be attributed to asymmetric stretching vibrations of un-ionized COOH and ionized COO$^-$ carbonyl groups and/or C=$\equiv$C bonds of sp$^2$ carbon respectively [8,33,34].

The weak intensity band at 1413 cm$^{-1}$ is attributed to symmetric stretching of COO$^-$ carbonyl, whereas the band at 745 cm$^{-1}$ to bending vibration of C=O bonds of the same group. Finally, the broad band between 1500 and 900 cm$^{-1}$ is assigned to O–H deformations of the C–OH groups as well as to O–C stretching vibrations [35,36].

On the other hand, the spectrum of the OMCN hybrid exhibits remarkable differences in comparison to that of the pristine nanosheets, which can be attributed to the successful functionalization of their surface. For instance, the spectrum of OMCNs appears to have new absorption bands at 457, 760, 914, 1043 and 1106 cm$^{-1}$ which can be attributed to Si=$\equiv$O, Si–O–Si and Si–OH vibrations of the inorganic part of AAPTMS [37]. However, the comparison with the spectrum of AAPTMS reveals a number of differences in the peak frequencies positions and in the intensities of the various bands, all
of which originate from vibrations of the silane CH3 groups. Especially the bands at 1195 cm\(^{-1}\) and 1085 cm\(^{-1}\) in the spectrum of AAPTMS, which are due to rocking vibrations of the C–H bonds and to stretching vibrations of C–O bonds of methoxy groups respectively, are not observed in the spectrum of the OMCN hybrid. The absence of these bands in the OMCN spectrum can be assigned to the silanization of carbon sheets through the creation of Si–O–Si or Si–O–C bridges.

Furthermore, in accordance with the above assignments, the appearance of a shoulder at about 1043 cm\(^{-1}\) is probably originating from the stretching vibrations of C–O–Si bonds. It is also interesting to note that the 1720 cm\(^{-1}\) band – assigned to vibrations of carboxyl groups – shifts to 1702 cm\(^{-1}\) and decreases in intensity. This difference indicates that the AAPTMS molecules condense with the OH groups of the carbon sheets, with the release of methanol and therefore the intensity of carboxyl band is decreased. Moreover, the band at 1618 cm\(^{-1}\) exhibits considerably larger bandwidth than the corresponding band in the spectrum of pristine material. This is due to the overlap with the absorption vibrations of NH\(_2\) groups (1660 cm\(^{-1}\) asymmetric stretch, 1577 cm\(^{-1}\) deformation).

The Raman spectra of pristine and OMCN hybrid are shown in Fig. 2. Both spectra exhibit D band (1385 cm\(^{-1}\)) and G band (1600 cm\(^{-1}\)), both being characteristic fingerprints of all carbon materials with a defect graphite structure [16,17,38]. Accordingly, the high frequency band at 1600 cm\(^{-1}\) is indicative of sp\(^2\)-hybridized carbons, while the weaker in intensity band at 1385 cm\(^{-1}\) originates from sp\(^3\)-hybridized carbons. As previously reported [30], the spectral characteristics of pristine material suggest the formation of long-range graphitized carbon with a relatively small number of structural defects, the latter pertaining to vacancies, morphological sheet distortions (folding, twisting etc.) and the presence of heteroatoms (H, O and N). The only difference observed in the spectrum of hybrid material (OMCNs) is the higher relative intensity of D band to G band. More specifically, the I\(_D\)/I\(_G\) ratio increases from 0.74 for pristine material to 0.88 for hybrid, suggesting an increase in the concentration of structural defects, probably due to the formation of new bonds between carbon atoms and organosilica molecules of AAPTMS. However, this relatively small increase reflects that the basic structure of carbon nanosheets in the hybrid remains intact after the functionalization process.

Fig. 2 shows the DTA/TG curves, recorded under air, of the carbon nanosheets before and after functionalization. The DTA curve of pristine material shows only an exothermic peak at 489 °C due to the oxidation of nanosheets. In contrast, in the DTA curve of OMCNs, two exothermic peaks are observed. The first dominant peak at 500 °C is also due to the oxidation of carbon nanosheets. The observed shift of the exothermic peak to higher temperature (+1 °C) can be attributed to silica moieties which cover the nanosheet surface of the OMCN hybrid. The second exothermic peak at 330 °C in the DTA curve of the hybrid could be attributed to the loss of AAPTMS molecules bonded to carbon sheets. From the difference in weight loss in the TG curves of two samples it is calculated that the AAPTMS functional molecules correspond to about 9.6 wt% of the total mass of OMCNs (the loading is ~1.6 mmol/g).

TEM images in Fig. 3 show the original sheets prepared by thermal decomposition of betaine (Fig. 4 pristine) as well as the sheets of the OMCN hybrid, i.e. after the surface functionalization (Fig. 4 OMCNs). As previously reported by Bourlinos et al. [30], the direct pyrolysis of betaine resulted in ultrathin carbonaceous nanosheets having the thickness around 6 nm and lateral dimensions in the range of 1–5 μm. On the other hand, the functionalization of pristine materials leads to the development of well-dispersed organosilica nanoparticles on graphitized surface of OMCN hybrid as depicted in Fig. 4 OMCNs. Evidently, the spherical particles cover the surface homogeneously and range between 3 and
15 nm in size. Moreover, the organic fraction is observable around individual nanoparticles as evidenced by high resolution image in Fig. 5.

We believe that this fraction would correspond to amino organosilica species formed after the functionalization procedure. Thus these species act as the bridge between the pristine carbon surface and spherical organosilica nanoparticles as well as they can cover the original carbon layer as isolated molecules. The general chemical model constructed on the basis of the above mentioned results is depicted in Fig. 5.

3.2. Surface properties of nanosheets and characterization of nanoparticles

A solid-state X-band EPR spectrum for the pristine material is presented in Fig. 6. The spectrum is characteristic of a strong free-radical signal with $g = 2.0036$ and a linewidth of $\Delta H_{pp} = 4.5$ Gauss. Spin-concentration, determined using DPPH as a spin standard [39], showed that the pristine material contained $8.9 \times 10^{15}$ spins [i.e. $1.36 \times 10^{-2}$ nmol] per gram of material. These properties are summarized in Table 1.
The Gaussian line-shape implies an inhomogeneous broadening mechanism due to the site inhomogeneity. The present EPR data manifest that the unpaired spins have restricted mobility on the carbon material. Similar signals have been also recorded for other carbon-based materials, like graphitic nanoparticles, carbon nanofoam, nanohorns [40–42] or in a carbonaceous material formed by solid-state pyrolysis of acetylenedicarboxylic acid [43].

The g-value (2.0036), is higher than the g-values for graphitic nanoparticles (g = 2.0023), nanofiber (g = 2.0029–2.0032) or nanohorns (g = 2.0023). This indicates delocalization of the unpaired spin on heteroatoms such as N atoms or O atoms of OH groups of the carbon sheets. The microwave saturation profile indicates a \( P_{1/2} \) value \( (P_{1/2} = 0.30 \text{ mW at } 77 \text{ K}) \) which implies a relatively weak coupling of the unpaired spin with lattice phonons. As a comparison, the radical centers formed on the carbonaceous material formed by solid-state pyrolysis of acetylenedicarboxylic acid [43] showed a significantly higher \( P_{1/2} \) value \( (P_{1/2} = 0.68 \text{ mW at } 77 \text{ K}) \) due to strong implication of oxygen orbitals in the radical stabilization.

Noticeably the solid-state X-band EPR spectrum for the OMCN hybrid was characterized also by strong free-radical signals; their characteristics are summarized in Table 1. Thus the grafting procedure did not destroy the radical centers, instead a drastic increase was observed. From the spin counting data (Table 1) more than 110% increase of the stable radical was observed in the OMCN material vs. the unmodified nanosheets. Moreover, compared with the reference material, a small – however resolvable – upshift of the g-value e.g. \( g = 2.0038 \) and a linewidth increase \( \Delta H_{\text{pp}} = 5.1 \text{ Gauss} \), was observed in the OMCN hybrid. These changes show that the radical sites are modified to a limited degree by the grafting treatment.

![EPR spectrum of the pristine material at 77 K](image)

Fig. 6. EPR spectrum of the pristine material at 77 K. Experimental conditions: microwave frequency 9.44GHz, modulation amplitude 1.00G, microwave power 22dB. [Solid squares]: estimation of the saturation parameter \( P_{1/2} \) by progressive microwave saturation profile at 77 K.

(i) The hyperfine features marked in Fig. 7 are typical for mononuclear Cu(II) \((S = 1/2, I = 3/2)\) complexes [46]. The spectrum can be simulated assuming a spin system with \( S = 1/2, I = 3/2 \) i.e. for Cu(II), by using the g and A tensor I with \((g_x, g_y, g_z) = (2.068, 2.031, 2.230)\) and \((A, A_x, A_y) = (13.0, 13.0, 186.0 \text{ Gauss})\). Analysis of the Az and gz values can give detailed quantitative information on the coordination environment of Cu(II) ions. In this context, the \( Az \) vs \( g_z \) correlation plot offers an appropriate method [47]. By comparison with literature data [47], the present Az and gz values reflect that bound Cu(II) ions are strongly coordinated by 2N and 20 atoms. The linewidth of the hyperfine lines in Fig. 7 is indicative of significant broadening due to spin-spin interactions between neighboring mononuclear Cu(II) complexes [31]. By analysing the linewidth and the relative intensity of the ratio of allowed/forbidden EPR transitions by the method developed by Grigoropoulos et al. [31], the Cu-Cu distance is estimated to be \( R_{[\text{Cu-Cu}]} = 4–5 \) Angstroms.

(ii) A broad background signal in Fig. 7 manifests that strong Cu-Cu couplings are also occurring in the OMCNs–Cu(II) material. This type of interactions results in unresolved linewidth broadening extending over hundreds of Gauss [48]. This proves the formation of Cu-clusters on the surface of the OMCNs–Cu(II) material. Overall the EPR data for Cu(II) on the OMCN material show that Cu ions are bound in two types of surface conformations: (i) the Cu ions are mononuclear held together by N and O atoms at Cu–Cu distances of 4–5 Angstroms, (ii) strong agglomeration of Cu atoms occurs resulting in cluster formation.

<table>
<thead>
<tr>
<th>Material name</th>
<th>( P_{1/2} (\text{mW} \pm 0.05) )</th>
<th>g-value ( (\pm 0.0002) )</th>
<th>Linewidth (-\Delta H (\text{Gauss} \pm 0.2))</th>
<th>Spins ( (10^{11}/g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.30</td>
<td>2.0036</td>
<td>4.5</td>
<td>8.9</td>
</tr>
<tr>
<td>OMCNs</td>
<td>0.031</td>
<td>2.0038</td>
<td>5.1</td>
<td>23.8</td>
</tr>
<tr>
<td>OMCNs-Cu(II)</td>
<td>0.40</td>
<td>2.0038</td>
<td>5.1</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Table 1

EPR characteristics for the free-radical centers measured for the carbonaceous nanosheets.

It may, therefore, be concluded from the above structural and spectroscopic data that the as-synthesized and modified carbon nanosheets exhibit functionalities, due to the formed, covalently attached, AAPTMS molecules and highly dispersed organosilica nanoparticles on the nanosheets surfaces. Along these lines, the OMCNs can be regarded as promising nanomaterials since, due to their nanoscale level functionalization, their dispersion and interfacial properties could be enhanced and tuned. In addition, as a result...
of a thin platy morphology and amine functionalization, OMCNs may find applications in polymer nanocomposites, heavy metal uptake, CO\textsubscript{2} absorption or immobilization of biomolecules.

4. Conclusions

The direct pyrolysis of betaine at 400 °C in air, followed by a simple surface treatment using AAPTMS organosilane precursor under reflux conditions, leads to carbon nanosheets modified with organosilane molecules and decorated with amino-functionalized organosilica nanoparticles. The results showed that:

(a) The organosilica modified carbon nanosheets remain the unique nearly 2D morphology of the pristine carbonaceous material with the estimated loading of functionalizing molecules and organosilica nanoparticles around 10% of the total mass.

(b) The grafting treatment results in a significant increase (more than 100%) of the radical center concentration in the OMCN structure as proved by EPR. The grafting creates the C–O–Si bridges between carbon layers and the organosilica nanoparticles.

(c) Experiments using Cu\textsuperscript{2+} probe ions show that the organosilane functional groups have been dispersed at distances of about 4–5 Å on the hybrid surface. In addition, probe ion results show that there is a strong agglomeration of copper Cu\textsuperscript{2+} ions, due to the organosilane nanoparticle formation.

Generally, the developed functionalization procedure of the betaine-derived carbon nanosheets would be applicable for the surface modification of other carbon nanostructures including graphene and mesoporous carbon.

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References


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