DOI: 10.1002/chem.200903560

Polymer Covalent Functionalization of Carbon Nanohorns Using Bulk Free Radical Polymerization

Grigoris Mountrichas,*[a] Stergios Pispas,[a] Toshinari Ichihasi,[c] Masako Yudasaka,[b] Sumio Iijima,[b] and Nikos Tagmatarchis*[a]

Abstract: Herein, we report on a facile approach for the covalent functionalization of carbon nanohorns, using in situ bulk free radical polymerization of methacrylic acid. The obtained material is soluble in aqueous media, facilitating its processability and has been fully characterized by means of complementary spectroscopic techniques, electron microscopy, thermogravimetric analysis, and light scattering. Simultaneously, the material has been used as a template for the synthesis of gold nanoparticles on the surface of the polymer-decorated carbon nanohorns.

Keywords: carbon nanohorns · covalent functionalization · free radical polymerization · gold nanoparticles · polymers

Introduction

Carbon nanohorns (CNHs), a subclass within the carbon nanotube (CNT) family, consist of tubular graphene sheets with conical ends, which covalently interact with each other to form a secondary spherical superstructure, resembling the dahlia flower.[1] Due to their unique structure, CNHs have been already proposed for diverse nanotechnological applications, including gas adsorption and storage,[2] fuel cells,[3] and catalytic nanoparticle supports.[4] Moreover, CNHs are a promising material for biotechnological applications,[5] because they are a metal-catalyst-free material, in marked contrast to CNTs. However, like CNTs, a major drawback for CNHs is that they are not soluble in organic or aqueous media.

During the last few years, CNHs have been studied in terms of surface functionalization, which eventually allows dissolution in a variety of solvents or water.[6] Independent reports from our group and others,[7–12] focused on the covalent (either at the sidewalls or the conical tips) or noncovalent functionalization of CNHs, with low-molecular-weight organic compounds. Briefly, pyrrolidine-,[7] amine-,[8] aryl-,[9] and cyclopropane-functionalized[10] CNHs have been reported. Oxidized CNHs have also been prepared and condensed with amines, forming novel hybrid materials.[11] Additionally, CNHs have been solubilized upon noncovalent π–π interactions with aromatic flat molecules such as pyrenes and porphyrins.[12]

However, the polymer functionalization of CNHs has yet to be fully explored, as has been done for CNTs.[13] In particular, based on the grafting-to approach, only the covalent attachment of polyethylene oxide[14] and polyisoprene or polyisoprene-*b*-polystyrene[15] has been reported by our group. In the grafting-to methodology previously applied, polymer chains, already prepared, were attached to CNHs. Moreover, the synthetic protocols utilized require either the previous oxidation of the CNHs[14] or the use of demanding high-vacuum techniques.[15] On top of this, the polymers used to decorate the surface of CNHs contribute only to the solubilization of the carbon nanostructure and since they do not contain functional sites, the formation of a novel hybrid materials for further exploitation is not possible. To overcome such deficiencies, our group has prepared a “functional” poly[styrene-*b*-(sulfamate/carboxylate isoprene)] block polyelectrolyte (CSI), which has been subsequently utilized for decorating the surface of CNHs[16] and CNTs.[17] The block polyelectrolyte decorated CNHs were further used for the templated formation of gold nanoparticles to give rise to

---

[a] Dr. G. Mountrichas, Dr. S. Pispas, Dr. N. Tagmatarchis
Theoretical and Physical Chemistry Institute
National Hellenic Research Foundation
48 Vass. Constantinou Avenue, 11635, Athens (Greece)
Fax: (+30) 210-7273-794
E-mail: tagmatar@eie.gr
gmountri@eie.gr

[b] Dr. M. Yudasaka, Dr. S. Iijima
Nanotube Research Center
National Institute of Advanced Industrial Science
and Technology (AIST)
Central 5, 1-1-1 Higashi, Tsukuba 305-8565 (Japan)

[c] Dr. T. Ichihasi
NEC Corporation, 34 Miyukigaoka
Tsukuba 305-8501 (Japan)

CNH/CSI/Au nanohybrids.[16] In the case of the CNT/CSI nanosystem, CdS nanoparticles were formed in the polyelectrolyte corona of the carbon nanotube/block copolymer nanoassembly and the final CNT/CSI/CdS nanohybrid[17] obtained was exploited as a new active nanomaterial for the construction of a photoelectrochemical cell with about 7% incident photon to photocurrent efficiency.[18]

Herein, we describe a quick and facile protocol for the covalent functionalization of CNHs, using in situ bulk free radical polymerization of methacrylic acid. The formed polymer is a polyelectrolyte, offering a large number of ionic groups all around the skeleton of CNHs and thus facilitating water solubility. Moreover, we took advantage of these ionic sites to direct the synthesis of gold nanoparticles on the surface of the polymer-decorated hybrid material.

Results and Discussion

Covalent functionalization: The tendency of carbon structures, like carbon black, to react with free radicals has already been reported in the literature.[19,20] Moreover, it has been found that the induced radicals, on the CNTs by the free radical initiator, trigger the grafting of polymer chains.[21] The covalent functionalization of CNHs was performed by in situ bulk free radical polymerization of a vinyl monomer in the presence of the CNHs. This is a one-pot reaction, in which pristine CNHs are used in the reaction flask from the beginning. Additionally, it must be highlighted that the functionalization reaction proceeds quite fast and only commercially available reagents are used. The in situ synthesis of poly(methacrylic acid) (PMAA) in the presence of CNHs was performed in an inert atmosphere of N_2 to avoid deactivation of the radicals due to atmospheric oxygen. Initially, all the reagents (monomer, initiator, and CNHs) were introduced in a flask and the temperature was raised to 65 °C. It is well known that the initiator, 2,2′-azobisisobutyronitrile (AIBN), is homolytically decomposed at this temperature by eliminating N_2. The as-formed radicals could react either with the vinyl monomers, thus initiating the polymerization, or with CNHs. Subsequently, there are three possible and distinct scenarios: 1) the polymerization will be terminated by disproportionation of the growing polymer chains, 2) a growing polymer chain will covalently bind to the surface of the CNHs by attack of the active polymer chain end to the carbon skeleton, and 3) polymerization of the monomer by radicals present on the CNH surface. The above scenarios can take place simultaneously, leading to a mixture of free polymer chains and polymer-functionalized CNHs (Figure 1). Finally, after 15 min, the reaction mixture became solid and the reaction was terminated by exposing the reagents and the products to atmospheric oxygen, where all existing radicals are deactivated. The obtained crude reaction product gives stable ink-like solutions in methanol and in basic aqueous media (pH 12). The aforementioned stable colloidal solutions are indirect evidence of the successful preparation of the hybrid nanomaterial.

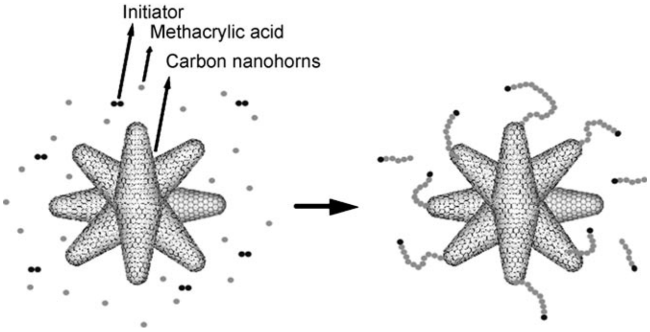

Figure 1. Illustration of the covalent functionalization of CNHs by in situ free radical polymerization of methacrylic acid.

To isolate and characterize the pure polymer-functionalized CNHs, part of the material was dissolved in aqueous media at pH 12, followed by extensive filtration through a Teflon membrane and subsequent washing with a large amount of solvent until no polymer could be detected in the filtrate. An aqueous solution of NaOH (pH 12) was used for washing the sample, since methanol is a toxic and volatile solvent. Moreover, at pH 12, the polymeric carboxylic acid side groups are in their dissociated form as carboxylate groups. In this form, the development of hydrogen bonds between the carboxylic groups is limited; therefore, removing the free polymer chains is easier. It is important to mention that, because of the solvent used for the purification of the sample, the covalently attached chains on CNHs are in the sodium salt form in the final purified material.

The purified polymer-functionalized material, namely, CNH–PMAA, the crude reaction product, CNH–PMAA with free PMAA, as well as the isolated free polymer, PMAA, were characterized with the aid of a number of complementary spectroscopic, thermal, and microscopy techniques. The UV/Vis-NIR spectra of the above materials, in aqueous solution, at pH 12, are given in Figure 2. The recorded spectra indicate that the CNH-containing samples

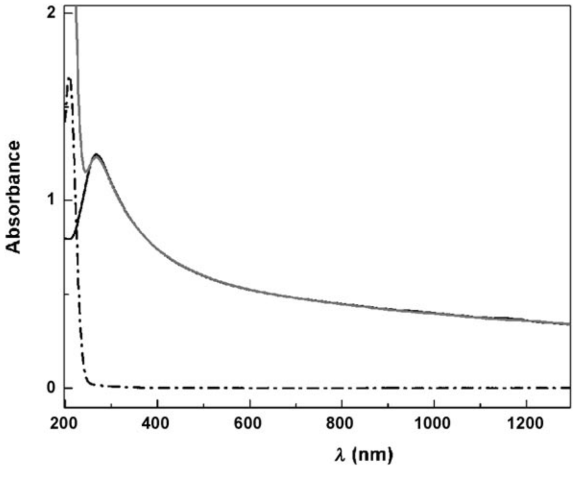

Figure 2. UV/Vis-NIR spectra of CNH–PMAA (black), crude reaction product (gray), and PMAA (dashed).

have a sloping baseline and a peak maximum at 270 nm, which is consistent with the structure of the CNHs.[14,15] Moreover, the PMAA sample shows no absorbance in the whole spectrum, with the only exception at the high energy range, where a large absorption is observed. The same absorbance is also recorded in the crude reaction product, indicating the existence of free polymer chains in this sample. However, this absorbance is only partially observed in the spectrum of the hybrid CNH–PMAA, indicating that there is a relatively small amount of the polymer in the final hybrid nanomaterial (i.e., only the covalently attached PMAA chains are observed).

IR spectroscopy was also utilized. The recorded spectra of the materials are given in Figure 3. A general observation is that many of the intense signals, which are observed in the case of PMAA, are also recorded in the CNH-containing hybrid material. In particular, the signals at 1170, 1557, and 1695 cm^{-1}, attributed to C=O and C−O vibrations, indicate the existence of polymer chains in all samples investigated. Moreover, in the case of the hybrid CNH–PMAA, there is a slope in the baseline, which is a usual observation when carbon nanostructures are investigated.[14] However, no slope is observed in the spectra of the crude reaction product, something which can be probably explained by the relatively small amount of CNHs in this product.

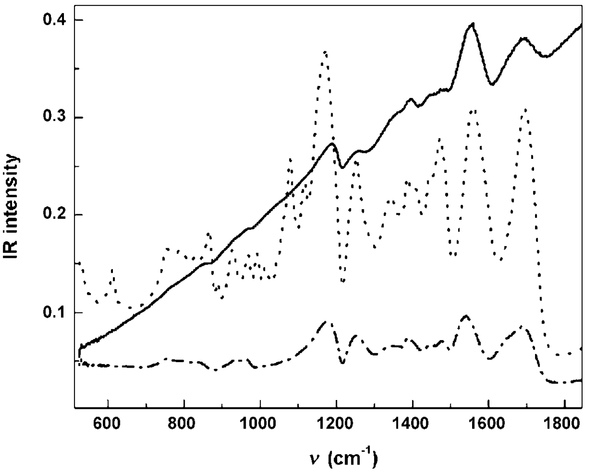

Figure 3. IR spectra of CNH–PMAA (black), crude reaction product (dashed), and PMAA (dotted).

In addition, Raman spectroscopy was also applied to prove the covalent nature of the functionalization. It is known that the Raman vibrational spectrum of the CNT family members, such as CNHs, has two bands, assigned as D and G bands, centered at 1272 and 1598 cm^{-1}, respectively. The G band is associated with the vibrations of sp^2-hybridized carbon atoms, whereas the D band is attributed to sp^3 single-bonding atoms and corresponds to the CNH core and the defect sites of the nanostructure. Upon covalent functionalization of CNHs, a number of defect sites are formed; therefore, an increase in the D band intensity is expected. However, as we have previously demonstrated in detail, for the covalent functionalization of CNHs with other macromolecular chains, the D band intensity is only slightly increased.[15] Indeed, this is the case when the Raman vibrational spectra of pristine CNHs and of CNH–PMAA are compared, as shown in Figure 4. Nevertheless, even this slight increase is attributed to an increase of the defect sites, which is the result of the covalent attachment of the polymer chains to the skeleton of the CNHs.

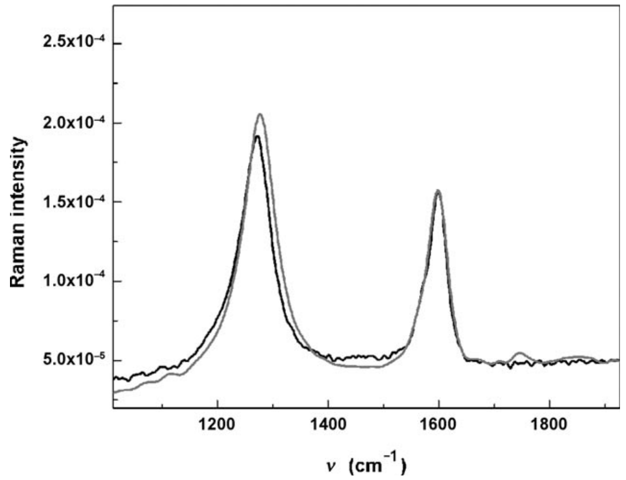

Figure 4. Raman spectra of pristine CNHs (black), and CNH–PMAA (gray), obtained with excitation at $\lambda_{exc} = 1064$ nm.

The amount of polymer in the samples can be easily calculated by performing thermogravimetric analysis (TGA) experiments. The results, which were obtained by TGA, are given in Figure 5. First, it has to be noted that CNHs are thermally stable at temperatures up to 600 °C, under an inert atmosphere. Therefore, the decrease in the sample weight, recorded for the pure CNH–PMAA and for the crude reaction product, is assigned to polymer decomposi-

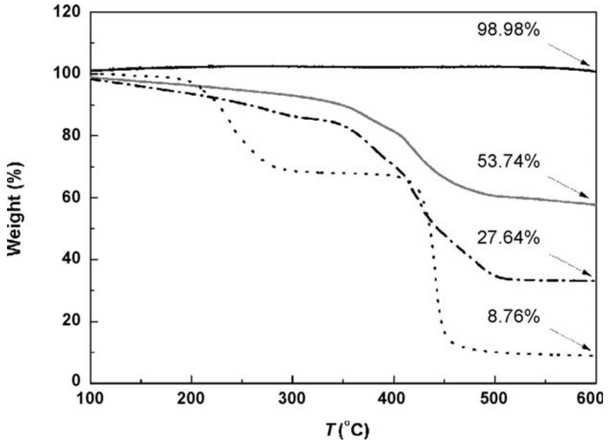

Figure 5. TGA thermographs of pristine CNHs (black), CNH–PMAA (gray), the crude reaction product (dashed), and PMAA (dotted), obtained under N_2.

tion. Consequently, the calculated polymer amount in the hybrid CNH–PMAA is about 50 wt%. However, since direct determination of the polymer molecular weight is not feasible, due to the presence of CNHs, the estimation of a number for the functionalized sites is not possible. Interestingly, the calculated polymer amount for the case of the crude reaction product is quite low, about 80 wt%. Considering that the initial weight ratio of monomer/CNHs was 100/1 the aforementioned result seems to overestimate the presence of CNHs. The above could be explained by considering a degree of monomer polymerization less than 100%, that is, there were monomers that were not polymerized, probably due to the presence of CNHs and to the limited polymerization time. However, at this stage it should be mentioned that, since the polymer is not completely decomposed at 600 °C, a corrected value was calculated for the determination of the polymer content.

The structural characterization of the nanohybrid CNH–PMAA was performed by HR-TEM. The recorded HR-TEM image, shown in Figure 6, indicates that the unique structure of the CNHs is retained after the covalent attachment of the polymer chains. In particular, the spherical shape of the assembly and the conical end of the tubes are all preserved in the functionalized material. Moreover, the overall size of the nanohybrid is measured to be about 100 nm, which is the same with that of pristine CNHs. However, parallel to the preservation of the basic structural characteristics of CNHs, the functionalized nanohybrid is soluble in aqueous media, in marked contrast to the pristine CNHs.

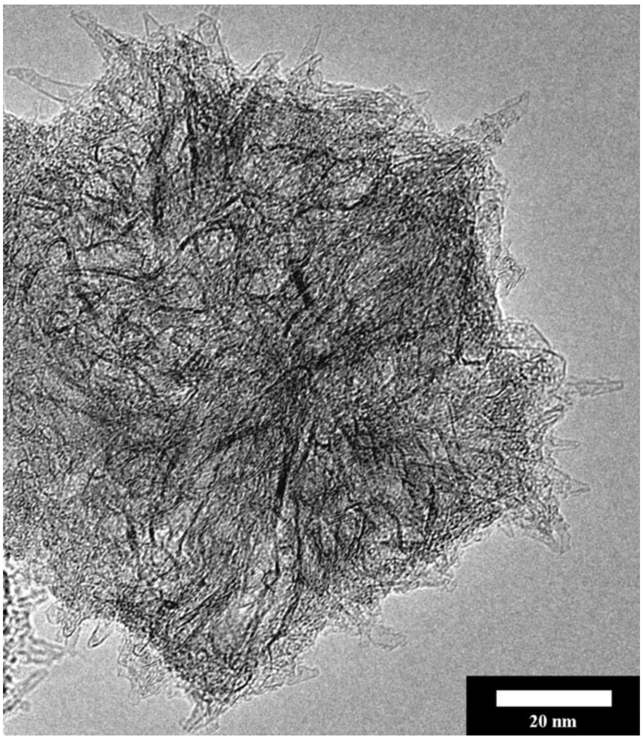

Figure 6. HR-TEM image of CNH–PMAA nanohybrid.

Deeper investigation of the structure of the material was achieved by dynamic light scattering (DLS), a technique that permits the characterization of the nanohybrid in aqueous solution.[22] Importantly, in contrast to elongated CNTs, DLS can be used in a more straightforward manner for CNHs, due to their secondary spherical aggregate structure. The measurements were performed on very diluted samples to avoid absorbance phenomena and to diminish the interaction between the nanohybrid particles. The results, as they have been analyzed by using the CONTIN algorithm, for a scattering angle of 90°, are given in Figure 7. Based on that, the apparent hydrodynamic radius (R_h) of the nanohybrid is about 160 nm. Moreover, there is only one dispersed population in the solution. The calculated apparent R_h of the sample is not comparable with that calculated by using HR-TEM. However, the above difference can be explained when considering that in DLS the apparent R_h is measured in solution and characterizes the overall size of the nanohybrid particles, that is, that of the carbon nanostructure, of the polymer chains and the hydrodynamic interactions between the polymer chains combined.[15,22] In contrast, when using HR-TEM, only the carbon framework of the CNHs in the solid phase is visible in the images, since isolated and expanded polymer chains are not observed with electron microscopy. However, the situation is completely different in solution, in which the polymer chains are expanded, changing the volume of the nanohybrid.

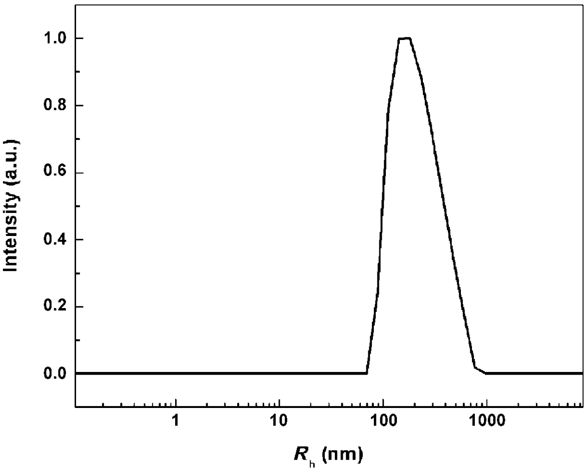

Figure 7. Hydrodynamic radius (R_h) distribution for CNH–PMAA in water, as obtained by Contin analysis of the correlation function for a scattering angle of 90°.

Gold nanoparticles loading onto CNH–PMAA: Gold nanoparticles have attracted the interest of the scientific community, mainly due to their exceptional optical and catalytic properties.[23] The synthesis of gold nanoparticles onto carbon nanotubes has been reported previously.[24] However, the use of highly pure CNHs, due to the absence of any metals, as well as the spherical superstructure of the CNHs considerably differentiates the new material from previously prepared ones based on CNTs. The synthesis of gold nanoparticles (Au_{NP}) was performed on the surface of the CNH–PMAA, to produce CNH–PMAA/Au_{NP} nanohybrids. This Au_{NP} preparation demonstrates the potential of the prepared CNH–PMAA material to act as a nanotemplate. Briefly, auric acid was added to CNH–PMAA and subsequently gold ions were reduced with the aid of hydrazine, similar to our previous methodology.[16] The UV/Vis absorption spectrum of the CNH–PMAA/Au_{NP} nanohybrid material after the addition of hydrazine is shown in Figure 8. The characteristic signal centered at 565 nm is attributed to the gold nanoparticles formed.[16] Moreover, based on the position and the width at half-height allowed to estimate the diameter of the nanoparticles to be approximately 3 nm. Additionally, the signal present at 310 nm is a redshift of the characteristic CNH absorption band, which is likely caused by interactions between the gold nanoparticles and the CNHs.[16]

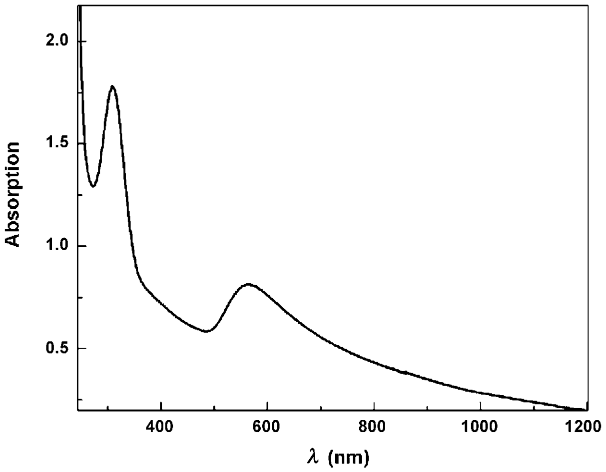

Figure 8. UV/Vis-NIR absorption spectrum of gold nanoparticles loaded onto CNH–PMAA, obtained in water.

The visualization of the gold nanoparticles attached to CNH–PMAA was performed by HR-TEM (Figure 9). The microscopy images indicated that the nanoparticles were formed on the CNH surface. Furthermore, the measured diameter of the nanoparticles (about 5 nm or less) is in good agreement with the one calculated above obtained by using the absorption spectroscopy measurements.

Finally, the successful synthesis of gold nanoparticles was also verified by energy-dispersive X-ray spectroscopy (EDX) measurements. The *Z*-contrast image and the corresponding EDX spectrum are given in Figure 10. The experimental results indicate the successful formation of the nanoparticles at the surface of the CNH–PMAA nanohybrid.

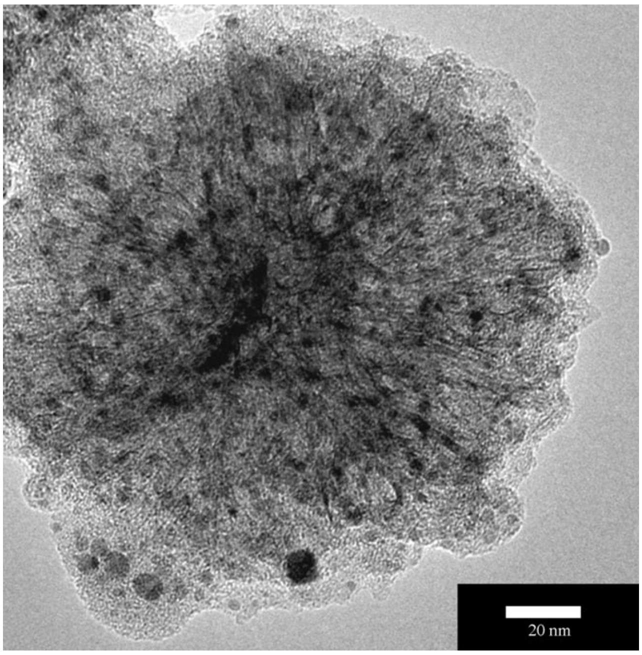

Figure 9. HR-TEM image of the gold nanoparticles loaded onto CNH–PMAA.

Conclusion

The fast, one-pot synthesis of covalent polymer-functionalized CNHs is described herein. The covalent approach has been realized by in situ bulk free radical polymerization of a methacrylic acid in the presence of CNHs leading to water-soluble CNH–PMAA nanohybrids. The hybrid material is characterized by using a wide gamut of techniques, which indicate the coexistence of polymer and CNHs in the final hybrid and the preservation of CNH structural characteristics. Finally, CNH–PMAA was used as a template for the synthesis of gold nanoparticles by reduction of gold ions. In particular, gold nanoparticles were localized at the periphery of polymer-decorated CNHs, as a result of complexation between negatively charged polymer chains and gold ions.

Experimental Section

Materials: Carbon nanohorns were synthesized from pure graphite targets by CO_2 laser ablation of graphite in the absence of any metal catalyst under an inert Ar atmosphere (760 torr) at room temperature.[1] The solvents and monomers utilized were purchased from Aldrich and used without further purification.

Covalent functionalization: The covalent attachment of polymethacrylic acid onto the side walls of the CNHs was realized by in situ bulk free radical polymerization of methacrylic acid in the presence of CNHs. In particular, methacrylic acid (3.2 g), AIBN initiator (1.8 mg) and CNHs (32 mg) were inserted in a round-bottomed flask equipped with a rubber septum. Subsequently, the temperature was raised to 65 °C and the reaction took place under an inert nitrogen atmosphere. The reaction was stopped after 15 min by exposing the reaction mixture to the atmosphere. The product of the reaction was a black solid, which was dissolved in alkaline aqueous solution (NaOH, pH 12). This solution was separated in

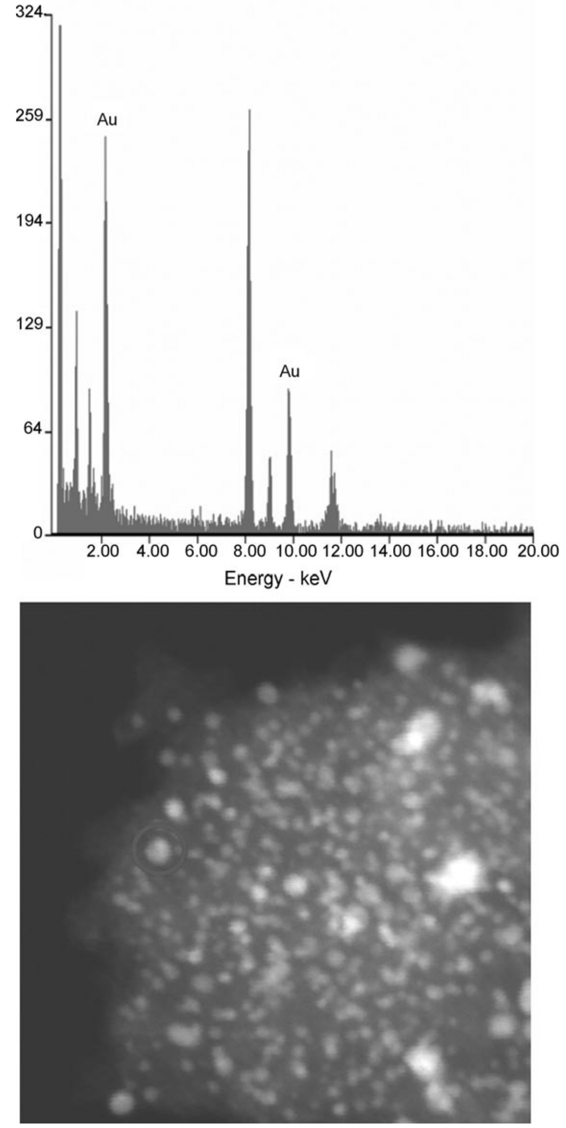

Figure 10. EDX spectrum of gold nanoparticles loaded onto CNH–PMAA (upper panel). The spectrum was measured in the gray area, shown on the *Z*-contrast scan image of the nanohybrid (lower panel). The signals other than Au are due to Cu, Fe, Al, and Si, which were present in the microscope equipment, sample holder, and crystal detector.

two parts. In the first one the solvent and the unreacted monomers were removed by evaporation under vacuum (crude reaction product). The second one was filtered through a Teflon membrane with 100 nm mean pore diameter and washed with large amounts of distilled water to remove the free polymer chains (purified CNH–PMAA).

Synthesis of gold nanoparticles: The synthesis of the gold nanoparticles was performed at the surface of polymer-functionalized CNHs. In particular, an amount of bulk gold was dissolved in a concentrated solution of HCl/HNO_3 (3/1 v/v) leading to a 0.3 M auric acid solution. Subsequently, an amount of the above solution (100 μL) was added to a dilute solution of the polymer-decorated carbon nanostructure (5 mL). This solution was left to stand overnight for equilibration. Afterwards, a catalytic amount of hydrazine was added for reducing the gold ions to metal nanoparticles.

Instrumentation: HR-TEM imaging was carried out by using a 002B Topcon electron microscope operated at an accelerating voltage of 120 kV. EDX analysis was performed on a scanning transmission electron microscope (HITACHI HD-2300) equipped with an EDX measurement system. The UV/Vis spectra of the samples were recorded by using a Perkin–Elmer (Lambda 19) spectrometer. Mid-infrared spectra in the region 550–4000 cm^{-1} were obtained on a Fourier Transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). Typically, 100 scans were acquired at 4 cm^{-1} resolution. Raman spectra were measured on a Fourier transform instrument (RFS 100 by Bruker Optics) employing approximately 350 mW of the Nd:YAG 1064 line in a back-scattering geometry. The spectra were measured at 2 cm^{-1} resolution and typically represent averages of 11000 scans (11 sets of 1000 scans). Thermogravimetric analysis of the sample was accomplished by using a TGA Q-500 instrument (TA Instruments) with a heating rate of 10 °C min^{-1}. Light scattering experiments were performed on a ALV/CGS-3 Compact Goniometer System (ALV GmbH, Germany), using a JDS Uniphase 22 mW He–Ne laser, operating at 632.8 nm, interfaced with a ALV-5000/EPP multi-tau digital correlator with 288 channels and a ALV/LSE-5003 electronics unit for stepper motor drive and limit switch control.

Acknowledgements

Partial financial support from the EU FP7, Capacities Program, NANOHOST project (GA 201729) is acknowledged.

---

[1] S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, K. Takahashi, *Chem. Phys. Lett.* **1999**, *309*, 165–170.

[2] a) K. Murata, K. Kaneko, F. Kokai, K. Takahashi, M. Yudasaka, S. Iijima, *Chem. Phys. Lett.* **2000**, *331*, 14–20; b) K. Murata, K. Kaneko, H. Kanoh, D. Kasuya, K. Takahashi, K. Kokai, M. Yudasaka, S. Iijima, *J. Phys. Chem. B* **2002**, *106*, 11132–11138; c) T. Ohba, T. Omori, H. Kanoh, M. Yudasaka, S. Iijima, K. Kaneko, *Chem. Phys. Lett.* **2004**, *389*, 332–336.

[3] a) E. Bekyarova, K. Murata, M. Yudasaka, D. Kasuya, S. Iijima, H. Tanaka, H. Kahoh, K. Kaneko, *J. Phys. Chem. B* **2003**, *107*, 4681–4684; b) N. Sano, S. Ukita, *Mater. Chem. Phys.* **2006**, *99*, 447–450.

[4] a) E. Bekyarova, A. Hashimoto, M. Yudasaka, Y. Hattori, K. Murata, H. Kanoh, D. Kasuya, S. Iijima, K. Kaneko, *J. Phys. Chem. B* **2005**, *109*, 3711–3714; b) T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kubo, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka, S. Iijima, *Physica B* **2002**, *323*, 124–126; c) T. Itoh, H. Danjo, W. Sasaki, K. Urita, E. Bekyarova, M. Arai, T. Imamoto, M. Yudasaka, S. Iijima, H. Kanoh, K. Kaneko, *Carbon* **2008**, *46*, 172–175; d) N. Karousis, T. Ichihashi, M. Yudasaka, S. Iijima, N. Tagmatarchis, *J. Nanosci. Nanotechnol.* **2009**, *9*, 6047–6054.

[5] a) T. Murakami, K. Ajima, J. Miyawaki, M. Yudasaka, S. Iijima, K. Shiba, *Mol. Pharm.* **2004**, *1*, 399–405; b) K. Ajima, M. Yudasaka, T. Murakami, A. Maigné, K. Shiba, S. Iijima, *Mol. Pharm.* **2005**, *2*, 475–480; c) J. Miyawaki, M. Yudasaka, H. Imai, H. Yorimitsu, H. Isobe, E. Nakamura, S. Iijima, *Adv. Mater.* **2006**, *18*, 1010–1014; d) X. Fan, J. Tan, G. Zhang, F. Zhang, *Nanotechnology* **2007**, *18*, 195103; e) S. Matsumura, K. Ajima, M. Yudasaka, S. Iijima, K. Shiba, *Mol. Pharm.* **2007**, *4*, 723–729; f) T. Murakami, J. Fan, M. Yudasaka, S. Iijima, K. Shiba, *Mol. Pharm.* **2006**, *3*, 407–414; g) J. Miyawaki, M. Yudasaka, T. Azami, Y. Kubo, S. Iijima, *ACS Nano* **2008**, *2*, 213–226; h) S. Lacotte, A. García, M. Décossas, W. T. Al-Jamal, S. Li, K. Kostarelos, S. Muller, M. Prato, H. Dumortier, A. Bianco, *Adv. Mater.* **2008**, *20*, 2421–2426; i) M. Zhang, T. Murakami, K. Ajima, K. Tsuchida, A. S. D. Sandanayaka, O. Ito, S. Iijima, M. Yudasaka, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 14773–14778; j) K. Ajima, T. Murakami, Y. Mizoguchi, K. Tsuchida, T. Ichihashi, S. Iijima, M. Yudasaka, *ACS Nano* **2008**, *2*, 2057–2064; k) T. Murakami, H. Sawada, G. Tamura, M. Yudasaka, S. Iijima, K. Tsucbida, *Nanomedicine* **2008**, *3*, 453–463; l) J. Miyawaki, S. Matsumura, R. Yuge, T. Murakami, S. Sato, A. Tomida, T. Tsuruo, T. Ichihashi, T. Fujinami, H. Irie, K. Tsuchida, S. Iijima, K. Shiba, M. Yudasaka, *ACS Nano* **2009**, *3*, 1399–1406.

[6] a) G. Mountrichas, G. Pagona, G. Rotas, N. Karousis, S. Pispas, N. Tagmatarchis, *J. Nanostruct. Polym. Nanocomp.* **2007**, *3*, 28–34; b) G. Pagona, G. Mountrichas, G. Rotas, N. Karousis, S. Pispas, N. Tagmatarchis, *Int. J. Nanotechnol.* **2009**, *6*, 176–195.

[7] a) N. Tagmatarchis, A. Maigne, M. Yudasaka, S. Iijima, *Small* **2006**, *2*, 490–494; b) C. Cioffi, S. Campidelli, F. G. Brunetti, M. Meneghetti, M. Prato, *Chem. Commun.* **2006**, 2129–2131; c) G. Pagona, G. Rotas, I. D. Petsalakis, G. Theodorakopoulos, J. Fan, A. Maigne, M. Yudasaka, S. Iijima, N. Tagmatarchis, *J. Nanosci. Nanotechnol.* **2007**, *7*, 3468–3472; d) N. Rubio, M. A. Herrero, M. Meneghetti, Á. Díaz-Ortiz, M. Schiavon, M. Prato, E. Vázquez, *J. Mater. Chem.* **2009**, *19*, 4407–4413.

[8] a) H. Isobe, T. Tanaka, R. Maeda, E. Noiri, N. Solin, M. Yudasaka, S. Iijima, E. Nakamura, *Angew. Chem.* **2006**, *118*, 6828–6832; *Angew. Chem. Int. Ed.* **2006**, *45*, 6676–6680; b) C. Cioffi, S. Campidelli, C. Sooambar, M. Marcaccio, G. Marcolongo, M. Meneghetti, D. Paolucci, F. Paolucci, C. Ehli, G. M. A. Rahman, V. Sgobba, D. M. Guldi, M. Prato, *J. Am. Chem. Soc.* **2007**, *129*, 3938–3945; c) A. S. D. Sandanayaka, O. Ito, T. Tanaka, H. Isobe, E. Nakamura, M. Yudasaka, S. Iijima, *New J. Chem.* **2009**, *33*, 2261–2266.

[9] G. Pagona, N. Karousis, N. Tagmatarchis, *Carbon* **2008**, *46*, 604–610.

[10] S. P. Economopoulos, G. Pagona, M. Yudasaka, S. Iijima, N. Tagmatarchis, *J. Mater. Chem.* **2009**, *19*, 7326.

[11] a) G. Pagona, N. Tagmatarchis, J. Fan, M. Yudasaka, S. Iijima, *Chem. Mater.* **2006**, *18*, 3918–3920; b) G. Pagona, A. S. D. Sandanayaka, Y. Araki, J. Fan, N. Tagmatarchis, G. Charalambidis, A. G. Coutsolelos, B. Boitrel, M. Yudasaka, S. Iijima, O. Ito, *Adv. Funct. Mater.* **2007**, *17*, 1705–1711; c) A. S. D. Sandanayaka, G. Pagona, N. Tagmatarchis, M. Yudasaka, S. Iijima, Y. Araki, O. Ito, *J. Mater. Chem.* **2007**, *17*, 2540–2546; d) G. Rotas, A. S. D. Sandanayaka, N. Tagmatarchis, T. Ichihashi, M. Yudasaka, S. Iijima, O. Ito, *J. Am. Chem. Soc.* **2008**, *130*, 4725–4731; e) G. Pagona, A. S. D. Sandanayaka, T. Hasobe, G. Charalambidis, A. G. Coutsolelos, M. Yudasaka, S. Iijima, N. Tagmatarchis, *J. Phys. Chem. C* **2008**, *112*, 15735–15741; f) A. S. D. Sandanayaka, O. Ito, M. Zhang, K. Ajima, S. Iijima, M. Yudasaka, T. Murakami, K. Tsuchida, *Adv. Mater.* **2009**, *21*, 4366–4371.

[12] a) J. Zhu, M. Yudasaka, M. Zhang, D. Kasuya, S. Iijima, *Nano Lett.* **2003**, *3*, 1239–1243; b) G. Pagona, A. S. D. Sandanayaka, Y. Arakai, J. Fan, N. Tagmatarchis, M. Yudasaka, S. Iijima, O. Ito, *J. Phys. Chem. B* **2006**, *110*, 20729–20732; c) G. Pagona, J. Fan, A. Maigne, M. Yudasaka, S. Iijima, N. Tagmatarchis, *Diamond Relat. Mater.* **2007**, *16*, 1150–1153; d) G. Pagona, A. S. D. Sanadanayaka, A. Maigne, J. Fan, G. C. Papavassiliou, I. D. Petsalakis, B. R. Steele, M. Yudasaka, S. Iijima, N. Tagmatarchis, O. Ito, *Chem. Eur. J.* **2007**, *13*, 7600–7607.

[13] a) D. Priftis, G. Sakellariou, D. Baskaran, J. W. Mays, N. Hadjichristidis, *Soft Matter* **2009**, *5*, 4272–4278; b) D. Priftis, N. Petzetakis, G. Sakellariou, M. Pitsikalis, D. Baskaran, J. W. Mays, N. Hadjichristidis, *Macromolecules* **2009**, *42*, 3340–3346; c) G. Sakellariou, H. N. Ji, J. W. Mays, D. Baskaran, *Chem. Mater.* **2008**, *20*, 6217–6230; d) T. Hasan, Z. Sun, F. Wang, F. Bonaccorso, P. H. Tan, A. G. Rozhin, A. C. Ferrari, *Adv. Mater.* **2009**, *21*, 3874–3899; e) M. S. Strano, *Nat. Mater.* **2006**, *5*, 433–434.

[14] G. Mountrichas, N. Tagmatarchis, S. Pispas, *J. Nanosci. Nanotechnol.* **2009**, *9*, 3775–3779.

[15] G. Mountrichas, S. Pispas, N. Tagmatarchis, *Chem. Eur. J.* **2007**, *13*, 7595–7599.

[16] G. Mountrichas, T. Ichihashi, S. Pispas, M. Yudasaka, S. Iijima, N. Tagmatarchis, *J. Phys. Chem. C* **2009**, *113*, 5444–5449.

[17] a) G. Mountrichas, S. Pispas, N. Tagmatarchis, *Small* **2007**, *3*, 404–407; b) G. Mountrichas, N. Tagmatarchis, S. Pispas, *J. Phys. Chem. B* **2007**, *111*, 8369–8372.

[18] G. Mountrichas, A. S. D. Sandanayaka, S. P. Economopoulos, S. Pispas, O. Ito, T. Hasobe, N. Tagmatarchis, *J. Mater. Chem.* **2009**, *19*, 8990–8998.

[19] a) M. Ley, M. Szwarz, *J. Chem. Phys.* **1954**, *22*, 1621–1622; b) X. Lou, C. Detrembleur, V. Sciannamea, C. Pangnoulle, R. Jerome, *Polymer* **2004**, *45*, 6097–6102; c) X. Lou, C. Detrembleur, V. Sciannamea, C. Pangnoulle, R. Jerome, *Adv. Mater.* **2004**, *16*, 2123–2127; d) V. Datsyuk, C. G-Piecourt, S. Dagreou, L. Billon, J.-C. Dupin, E. Flahaut, A. Peigney, C. Laurent, *Carbon* **2005**, *43*, 873–876; e) J. Chen, H. Iwata, N. Tsubokawa, Y. Maekawa, M. Yoshida, *Polymer* **2002**, *43*, 2201–2206.

[20] a) X. Li, W. Guan, H. Yan, L. Huang, *Mater. Chem. Phys.* **2004**, *88*, 53–58; b) D. Yang, J. Hu, C. Wang, *Carbon* **2006**, *44*, 3161–3167; c) M. Liu, T. Zhu, Z. Li, Z. Liu, *J. Phys. Chem. C* **2009**, *113*, 9670–9675.

[21] S. J. Park, M. S. Cho, S. T. Lim, H. J. Choi, M. S. Jhon, *Macromol. Rapid Commun.* **2003**, *24*, 1070–1073.

[22] a) *Light Scattering from Polymer Solutions* (Ed.: M. B. Huglin), Academic Press, New York, **1972**; b) I. Teraoka, *Polymer Solutions*, Wiley, New York, **2002**; c) B. J. Berne, R. Pecora, *Dynamic Light Scattering*, Plenum Press, New York, **1976**; d) B. Chu, *Laser Light Scattering*, 2nd ed, Academic Press, New York, **1991**.

[23] a) M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293–346; b) R. Sardar, A. M. Funston, P. Mulvaney, R. W. Murray, *Langmuir* **2009**, *25*, 13840–13851.

[24] a) A. Tello, G. Cardenas, P. Haberle, R. A. Segura, *Carbon* **2008**, *46*, 884–889; b) T. Sainsbury, J. Stolarczyk, D. Fitzmaurice, *J. Phys. Chem. B* **2005**, *109*, 16310–16325; c) J. Hu, J. Shi, S. Li, Y. Qin, Z. X. Guo, Y. Song, D. Zhu, *Chem. Phys. Lett.* **2005**, *401*, 352–356; d) H. C. Choi, M. Shim, M. Bangsaruntip, H. Dai, *J. Am. Chem. Soc.* **2002**, *124*, 9058–9059; e) B. M. Quinn, C. Dekker, S. G. Lemay, *J. Am. Chem. Soc.* **2005**, *127*, 6146–6147; f) T. M. Day, P. R. Unwin, N. R. Wilson, J. V. Macpherson, *J. Am. Chem. Soc.* **2005**, *127*, 10639–10647; g) C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, Y. Yan, *Nano Lett.* **2004**, *4*, 345–348; h) P. Xu, X. Ji, H. Yang, J. Qi, W. Zheng, V. Abetz, S. Jiang, J. Shen, *Mater. Chem. Phys.* **2010**, *119*, 249–253; i) X. Tan, W. Deng, M. Liu, Q. Zhang, Y. Wang, *Chem. Commun.* **2009**, 7179–7181.

Received: December 28, 2009