Chemical Functionalization of Carbon Nanotubes and Derived Hybrids: Synthesis, Characterization and Study of Hydrogen Adsorption

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ABSTRACT

In the first part of the present PhD thesis, novel chemical routes for the chemical functionalization of single- and/or multi-wall carbon nanotubes were developed. The strategies that were adopted toward this aim, involved (i) The covalent attachment of chemical groups or derivatives using appropriate reactions (e.g. 1,3-dipolar cycloaddition) (ii) The immobilization of radicals (e.g. tyrosinate radical) on the graphitic surface of carbon nanotubes and (iii) The non-covalent attachment of suitable molecules (polyaromatic hydrocarbons e.g. amino-anthracene, pyrene-amine etc) on the surface of carbon nanotubes by π-π interactions.

In the second part of the thesis novel hybrid materials based on functionalized carbon nanotubes were developed and studied. Within this concept, various hybrid systems consisting of carbon nanotubes and bi-metallic (or monometallic) nanoparticles were synthesized since the combination of these two different categories of nanomaterials, may lead to the successful exploitation of their unique properties. In general, it was studied the capability to use the chemically modified surface of carbon nanotubes as nano-template where either nanoparticles directly grow and/or deposited or alternatively preformed nanoparticles attach by appropriate chemical interactions. In detail, there were synthesized novel hybrid materials of multiwalled carbon nanotubes and FePt nanoparticles by using the surface of nanotubes as nanotemplate for the dispersion and stabilization of the magnetic nanoparticles. The pre-formed capped FePt nanoparicles were connected to the chemical functionalized carbon nanotubes external surface via covalent binding through organic linkers. Using a similar methodology, pre-formed capped RuPt nanoparticles were immobilised for the first time on the external surface of chemical functionalized multi-wall carbon nanotubes via covalent interactions. Furthermore, the synthesis of novel hybrid materials consisting of γ-Fe_2O_3 nanoparticles, metallic Sn nanowires and multi-wall carbon nanotubes was exploited. Initially, Sn nanowires were grown by a catalytic chemical vapour deposition method along the inner cavity of multi-wall carbon nanotubes. The produced Sn nanowires-carbon nanotubes system was then decorated with the pre-formed capped Fe_2O_3 nanoparticles. Tin nanowires completely covered by carbon cells are protected from all sides against atmospheric oxidation (and hence are suitable for handling in air), while after a mild chemical functionalization on the

outer carbon wall suitable groups are imported which facilitate the immobilization of the nanoparticles.

Alternatively, it was studied the possibility of the direct development of nanoparticles on the surface of chemically functionalized carbon nanotubes. Single- and multi-wall carbon nanotubes were employed as nano-templates for the synthesis of various hybrid nanostructures consisting of carbon nanotubes and iron oxide nanoparticles (α-Fe_2O_3, γ-Fe_2O_3 or Fe_3O_4) via a simple, reproducible and versatile method. The strategy that was adopted involved the chemical functionalization of carbon nanotubes by two alternative routes, one targeting at the covalent functionalization of CNTs and the second one taking advantage of π-π interactions. CNT- nanoparticle composites were prepared by interaction of acetic acid vapors with iron cations dispersed on the surface of the derived functionalized nanotubes. Upon pyrolysis the created iron acetate species were transformed to magnetic iron oxide nanoparticles. The atmosphere which is used during the synthetic procedure affects significantly the nature of the nanoparticles which could be either γ-Fe_2O_3 or magnetite, or non-magnetic such as a-Fe_2O_3.

Novel hybrid systems of carbon nanotubes and layered silicates, in which the chemically functionalizied carbon nanotubes interact with either exfoliated or ordered clay platelets were developed using a simple synthetic route. Toward this method, homogeneous, coherent, and transparent clay-carbon nanotube composite films or gels are achieved by simple mixing colloidal solutions of nanotubes with clay dispersions. Finally, a novel composite hybrid system consisting of carbon nanotubes routed on smectite clays and γ-Fe_2O_3 nanoparticles was also synthesized and studied. Multi-wall carbon nanotubes were developed on the surfaces of clay platelets, using the catalytical chemical vapour deposition method. After purification, the carbon nanotube-clay composite materials were covalently functionalized in order to create the suitable chemical groups on the surface of nanotubes. In the final step, immobilizaation of the preformed capped γ-Fe_2O_3 nanoparticles took place on the surface of carbon nanotubes.

The chemical functionalization of carbon nanotubes that was studied in the first part of the thesis, as well as the synthesis of the various hybrid systems that followed in the second part, were studied in detail with a combination of experimental methods including: spectroscopic techniques (Raman, FT-IR, Mössbauer, UV-Vis, STS and EPR), thermal analysis (TGA-DTA), X-Ray diffraction measurements (XRD) and microscopies (TEM, AFM, STM και SEM). Finally, selected samples were evaluated for their ability to adsorb hydrogen under different conditions.