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Preparation of homogeneous titania coating on the surface of MWNT

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ABSTRACT

Preparation of homogeneous and stable inorganic coatings on the surface of multi-wall carbon nanotubes (CNTs) was studied. Precursor compounds such as titanium (IV) bromide and titanium (IV) chloride were used to cover the surface of CNTs under either solvent-free or solution conditions. As-prepared titania layers were characterized by transmission, scanning electron microscopy and X-ray diffraction techniques. Results revealed that homogenous coverage can be achieved in a controllable way.

1. Introduction

Multiphase materials containing nanoscale structures – so called nanocomposites – represent one of the most emerging area of nanotechnology. For their production, typically nanoparticles are dispersed into the matrix material during processing, and in a favorable case the resulting composite exhibits drastically enhanced properties than the matrix itself. For instance, adding carbon nanotubes (CNTs) into an epoxy considerably enhance its electrical and thermal conductivities as well as its mechanical properties such as stiffness and strength [1].

Besides conventional polymer composites (fiber reinforced: carbon or glass fiber, nylon, etc.), nanocomposites are expected to become multipurpose, industrial advanced materials. For this reason nanocomposites have been widely studied for the past 20 years. In particular, polymeric nanocomposites, where the high performance of polymers is combined with the advantages of nanomaterials, have advanced fast. Due to their unique structure with high aspect-ratio and anisotropic structure, CNTs represent ideal candidates for this kind of applications [2,3]. Using CNTs as reinforcement nanofibers, in the technological field of polymer nanocomposites promising results have been obtained [4,5]. However, the production of uniform nanocomposites with CNTs is a technical challenge as they preferentially agglomerate and do not disperse homogeneously. Moreover, due to the poor wetting of their surfaces obtaining a good interfacial bonding is a requirement in order to achieve efficient load transfer across the CNT–matrix interface, which is a necessary condition for improving the mechanical properties of the composite. Chemical functionalization of the CNT surface can damage its intrinsic structure. Formation of a proper coating on the surface of CNTs could offer an valuable alternative.

At the beginning of the nineties, the preparation of thin titania layer on activated carbon fiber (ACF) was investigated by molecular adsorption–deposition (MADD). In this work $TiCl_4$ and water were applied onto the ACF surface to obtain an oxide surface with specific activity. The TiO_2-coated ACF was characterized by thin-film X-ray diffraction and nitrogen adsorption, and the adsorption of water vapor, NO, and NH_3 was also measured [6]. In the last few years several publications appeared about the attachment of various inorganic compounds onto single-wall and multiple-wall CNTs. For example, oxide nanoparticles such as silica [7–10], tin oxide [11], alumina [12,13] and titania [14,15] have been successfully deposited onto the surface of CNTs by impregnation technique, chemical solution route or hetero-coagulation method. Coating was also obtained by a sol–gel method using classical alkoxides as $Ti(OEt)_4$ and $Ti(OPri)_4$ and by hydrothermal hydrolysis of $TiOSO_4$, leading to different TiO_2 morphologies [16]. With this technique nanotubes were coated either with a continuous TiO_2 layer or with TiO_2 nanoparticles depending on the applied precursor, $Ti(OEt)_4$ or $Ti(OPri)_4$ respectively. By subsequent hydrothermal treatment, more compact and crystalline nanocomposites could be obtained. Zhang et al. used $TiCl_4$ as starting material and

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demonstrated a method for coating single-walled CNTs by amine-terminated TiO_2 nanoparticles [17]. Pender et al. demonstrated that a multifunctional peptide could suspend SWNTs as individuals in solutions and precipitate silica or titania from water-soluble precursors at the surface of the nanotubes without covalent functionalization of the CNTs under mild conditions [18]. The relationship between the methods of synthesis and the properties of TiO_2 and the MWNT-nanocrystalline titania composite, such as surface area, particle size, pore volume and pore size distribution, crystal structure and crystallinity, bandgap energy, among others has been investigated in many studies [19,20]. Depending on the purpose, quality requirements for the coating may be different, however, mechanism of e.g. photocatalysis is still not classified. It is well known that titania is one of the most important semiconductors due to its high photocatalytic properties in the degradation of organic pollutants [21]. The major drawback in the practical application under irridation of solar light is the band gap energy (3.2 eV) for anatase TiO_2. Various efforts have been attempted to extend the light absorption of photocatalysts to the visible region [22,23]. Recently, nanosized TiO_2 deposited onto the surface of CNTs was found to shows excellent photocatalytic efficiency [24,25].

The electroless deposition method was also used for the coating of multi-wall CNTs (MWNTs). Before composite preparation MWNTs were shortened by long-time mechanical milling [26].

The amount of standalone inorganic particles cannot be controlled when using the solvent-free method for the preparation of MWNT based composite materials [9]. Consequently, a macroscopic sample contains a significant amount of various oxide materials as a side product. The aim of this work was to elaborate a controllable route to produce a stable inorganic layer on the surface of MWNTs. Using precursor compounds such as titanium bromide and chloride, fully covered MWNTs could be produced in large quantities without additional undesirable particles. Procedures were developed to form coatings on the surface of CNTs under either solvent-free or solution conditions. The resulting material can be used in further processes, for instance for CNT-based polymer composites and photocatalytic reactions as CNT–TiO_2 composite catalysts.

2. Experimental

2.1. Materials

MWNTs were prepared by the decomposition of acetylene (CVD method) in a rotary oven at 720 °C using Fe, Co/$CaCO_3$ catalyst [27]. This growth procedure using $CaCO_3$ catalyst support enables highly efficient selective formation of MWNTs without any amorphous carbon or carbonaceous particles [28] and yields MWNTs with a clean surface to create effective bonding between CNT and precursors.

Precursor molecules of titanium tetrachloride, $TiCl_4$ (Fluka) and titanium tetrabromide $TiBr_4$ (Aldrich) were used. Applied solvents are N,N-dimethyl-formamid, acetone, ethanol and toluene (all HPLC grade from Reanal).

2.2. Sample preparation

For the preparation of homogeneous titania layer on the surface of MWNT, two different methods were used. While some samples were prepared under solvent-free conditions, a series of composite materials were produced using the same precursors but in various solvents, namely toluene, acetone and ethanol.

Before the experiments purified MWNT was always dried in an oven at 100 °C for 60 min. Due to the extreme reactivity of the precursor molecules, all further manipulations were done under nitrogen atmosphere. For the solvent-free method, a calculated amount of precursor (either 12 mmol $TiCl_4$ or 6.8 mmol $TiBr_4$) and 0150 g MWNT was placed into a covered beaker without any solvent and was sonicated for 4×15 min at 45 °C. Subsequently, titanium compound was hydrolyzed by adding a few drops of distilled water to the mixture.

For sample preparation in various solvents, 0150 g MWNT was dispersed in 10 cm^3 of solvent, then the precursor was added to the suspension and sonicated for 4×15 min. We have selected these solvents in order to investigate their effect, in particular their dipole character, on the formation of the titania layer. The solubility of $TiBr_4$ precursor is better in each solvent we used than that of $TiCl_4$ precursor. The sonication was followed by hydrolysis again either in a fast step by adding 2 cm^3 water (fast hydrolysis) or in a slow step leaving the uncovered beaker in air (slow hydrolysis). After hydrolysis all samples were dried at 110 °C. In samples prepared with $TiCl_4$ and $TiBr_4$ precursors, the weight ratios of TiO_2: MWNT in the final product were 7:1 and 4:1, respectively.

2.3. Sample characterization – electron microscopy

For qualitative characterization, products were investigated by transmission electron microscopy (TEM, Philips CM10), in particular, to verify the formation of the inorganic coverage on the surface of MWNT. The TEM sample preparation involved grinding the material mechanically and gluing the ground powder on a Cu TEM-grid. High resolution transmission electronmicroscopy (HRTEM) characterization was carried out using a Philips CM300 FEG microscope operating at 300 kV. For HRTEM sample preparation, samples were dispersed in isopropanol and sonicated for 5 min. A droplet of suspension was put on a Cu TEM-grid with a holey carbon film. The presence of titania layer was confirmed by electron energy-loss spectroscopy (EELS) in scanning TEM (STEM) mode.

Observation of the inorganic layer by means of TEM is rather challenging because a low magnification is needed in order to verify the overall distribution of the inorganic material as well as the morphology of MWNTs. Whether MWNTs are indeed covered with the titania layer requires high-resolution TEM. However, as TEM provides images in projection a clear verification is not evident, in particular when the coating layer is thin. We particularly checked for the following direct or indirect "indicators" during TEM observations: bare ends of MWNTs "peeping out" of the layer (generally marked by an arrow in the figures); the contrast of the inner core of MWNT is significantly lower when covered; the surface of composite materials is less smooth. The thickness of the layer was determined by means of HRTEM by measuring the coverage on the MWNT surface.

Scanning electron microscopy (SEM) was done on a Hitachi S-4700 Type II FE-SEM equipped with a cold field emission gun operating in the range of 5–15 kV. The samples were mounted on a conductive carbon tape and sputter coated by a thin Au/Pd layer in Ar atmosphere prior to the measurement. Thermal analysis measurements were performed with Derivatograph Q (MOM) equipment. The crystalline structure of the inorganic layer was also studied by X-ray diffraction (Philips PW3710/PW 1050).

3. Results and discussion

3.1. Composite materials prepared under solvent-free conditions

In order to form titania coatings, MWNTs and titanium halogenide compounds were well homogenized in the absence of any