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ORIGINAL PAPER

Carbon nanotube–layered double hydroxide nanocomposites[‡]

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Preparation of multiwalled carbon nanotube–layered double hydroxide (MWCNT–LDH) nanocomposites by (i) the co-precipitation of LDH components and pristine or surface-treated MWCNT or (ii) the delamination of LDH and application of the layer-by-layer technique has been attempted. For MWCNT, two types of surface treatment were used, either the surface was hydroxylated and deprotonated or wrapped in a tenside (dodecylbenzenesulfonate, DBS). LDH was delaminated by *N*,*N*-dimethylformamide. The obtained materials were characterized by X-ray diffractometry (XRD), and by scanning and transmission electron microscopies (SEM and TEM). Element distribution was mapped with help of the X-ray energy dispersive spectroscopy (XEDS) available as an extension of the scanning electron microscope. MWCNT could not be sandwiched between the layers of LDH by any of the methods employed; however, tenside-treated bundles of MWCNT could be wrapped in LDH thus forming a nanocomposite.

Keywords: CaFe-layered double hydroxide, multiwalled carbon nanotube, composite, coating, sandwich-like structure

Introduction

The family of layered double hydroxides (LDHs) is a class of (mostly) synthetic anionic layered clays that can be represented by the general formula of $\left[\mathrm{M(II)}_{1-x}\mathrm{M(III)}_x(\mathrm{OH})_2\right]^{x+}[\mathrm{X}^{m-}_{x/m} \cdot n\mathrm{H_2O}]^{x-}$ (Cavani et al., 1991; Vaccari, 1998; Evans & Slade, 2006). Partial isomorphous substitution of divalent cations for trivalent ones results in positively charged layers balanced by simple, fully or partially hydrated, inorganic anions in the interlayer space. Their most often used representative is hydrotalcite (Brown & Gastuche, 1967), its layered structure resembles that of brucite [$Mg(OH)_2$], but a part of the Mg(II) ions is replaced by Al(III) ions. The metal cations occupy the centers of octahedra whose vertices are hydroxide ions. These octahedra are connected to each other by edge sharing to form an infinite sheet. When the divalent ion is Ca(II), the structure is somewhat different; it is the hydrocalumite type structure (Evans & Slade, 2006; Taylor, 1969; Rousselot et al., 2002; Vieille et al., 2004; Kim et al., 2012). Its parent structure is that of portlandite. Since the calcium ion is significantly larger than the magnesium ion (100 pm vs. 72 pm), it is heptacoordinated in hydrocalumites; thus, the layer consists of edge sharing heptacoordi-

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nated calcium hydroxide decahedra and hexacoordinated trivalent metal hydroxide octahedra.

The charge-compensating anions between the layers can be exchanged to more complex organic anions forming organic–inorganic functional nanocomposites (Pálinkó, 2006; Zümreoglu-Karan & Ay, 2012). These materials have many applications as immobilized organocatalysts (Choudary et al., 2002; An et al., 2006; Shi & He, 2011), protected organic moieties from unwanted transformations, e.g., racemization (Aisawa et al., 2001), targeted delivery of medicine with lengthened effects (Ambrogi et al., 2001), etc.

Although most varieties of LDHs can be found in nature, those for industrial application are usually synthesized. The most often used preparation method is the co-precipitation of the component salts using a base in solution (Duan et al., 2011).

Carbon nanotubes (CNTs) were discovered by Iijima while studying the growth of carbon nanostructures by the arc-discharge evaporation method (Iijima, 1991). Since then, it has been shown that carbon nanotubes can be derived from rolled-up carbon nanosheets. The tube can consist of one, two or more rolled-up sheets and thus they are accordingly called single-walled (SW), double-walled (DW), or multiwalled (MW) carbon nanotubes. Due to their peculiar mechanical, electrical as well as chemical properties, carbon nanotubes are in the center of research interest. Even though enthusiasm has lowered these days, hundreds of papers dealing with various aspects of carbon nanotube physics and chemistry appear every year.

There are many methods for the preparation of carbon nanotubes but the most efficient is the catalytic vapor deposition (CCVD). Thus prepared nanotubes have many vacancies and dislocations, i.e. their graphitic structure is by far not perfect (Dupuis, 2005). This can be a disadvantage as far as the mechanical properties are concerned (tensile strength of the tube is significantly lowered), and an advantage if hierarchical nanostructures are intended to be constructed since more interactions between these tubes and, e.g. LDHs, clays, or polymers of various kinds are possible (Zhao et al., 2012).

When nanostructures composed of CNTs and LDHs are concerned, the possibilities are as follows (Zhao et al., 2012): (i) CNTs uniformly attached on the surface of LDH flakes, (ii) intercalation of CNTs into the interlayer space of LDHs, (iii) in situ growth of LDHs on the surface of CNTs, (iv) randomly entangled CNTs grown from LDHs, (v) aligned CNT arrays grown from LDHs, and (vi) CNT-array double helix grown from LDHs. These types of hierarchical nanostructures have many uses; they can serve as electrodes, sensors as well as electric circuit elements after appropriate modification. However, working with these nanosized species requires considerable caution since they may constitute hazards to human health (Du et al., 2013).

In this contribution, our efforts to build MWCNT–LDH nanocomposites are described. The results of various methods (co-precipitation and the layer-by-layer technique) are described and discussed.

Experimental

For the synthesis of LDHs, $CaCl_2$ (98.1 %, puriss, Molar Chemicals, Hungary), $FeCl_3 \cdot 6H_2O$ (97.7 %, puriss, Molar Chemicals, Hungary), and NaOH (Reanal, Hungary) were used without further purification. Sodium dodecylbenzene sulfonate, DBS, (applied for various purposes like wrapping of multiwall carbon nanotubes, MWCNT, or indelamination) was purchased from Aldrich Chemical Co. (Hungary). *N*,*N*-Dimethylformamide (DMF, 99 %) and hexamethylenetetramine (hexamine, analytical grade) solvents for the delamination of LDHs were purchased from Merck (Hungary). The acids (cc. H_2SO_4 and fuming HNO_3) applied for treating MWCNTs were the products of Reanal (Hungary). MWCNT was synthesized in our laboratories via the chemical vapor deposition method. Millipore (Hungary) MilliQ water and N_2 gas (99.5 %) were used throughout the experiments.

Sample preparation was provided by the co-precipitation method (He et al., 2006). The first step of all synthetic experiments was the preparation of an acidic (pH = 1.7) solution containing $CaCl_2$ and $FeCl_3$ in a 3 : 1 molar ratio. The last step was setting the final pH to 13.

Three modifications of the co-precipitation method were tested. In method (A), 0.1–0.3 g of pristine or acid-treated MWCNT was added to 100 cm^3 of the above-described solution either with or without 0.3 g of DBS under N_2 atmosphere and the mixture was stirred for 30 min. After precipitation of the substances with 3 M NaOH, the samples were stirred at 80 °C for a week. In method (B), the pristine or acid-treated MWCNT (0.1–0.3 g) alone or together with DBS (0.3 g) were dispersed or dissolved in the amount of 3 M NaOH necessary for co-precipitation and the Ca(II) and Fe(III) ion containing solution was added dropwise under N_2 atmosphere and constant stirring maintained for an additional week at room temperature. In method (C), the acid-treated MWCNT was dispersed in 3 M NaOH by sonication (5 h) and the solution containing the salt mixture was added in one portion. Sonication was continued for additional 3 h. Then, stirring with a mechanical stirrer under N_2 atmosphere was applied for a week. All the samples were vacuum-filtered using a Versapor-129 (Hungary) membrane and kept in a desiccator over P_2O_5.

The aim of the acid treatment of MWCNT was to oxidatively generate hydroxylic and/or carboxylic groups containing more dislocations. Acid treatment with concentrated oxo acids partially destroys the nanotube structure through oxidation, attacking its

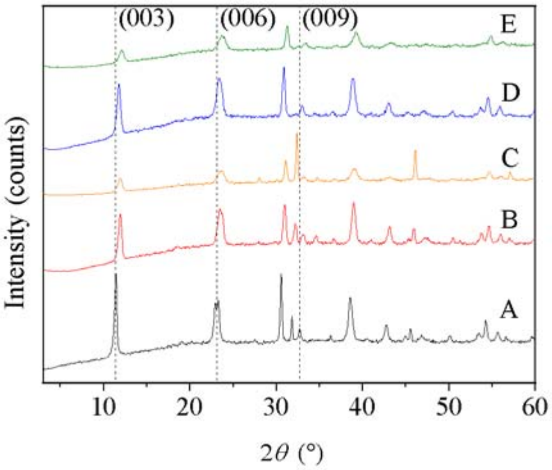

Fig. 1. X-ray diffractograms of CaFe-LDH (A), and composites of pristine MWCNT–CaFe-LDH (B), oxidatively treated MWCNT–CaFe-LDH (C), DBS–pristine MWCNT–CaFe-LDH (D), and DBS–oxidatively treated MWCNT–CaFe-LDH (E).

imperfections caused by the chemical vapor deposition method. Then, further dislocations bearing various oxygen-containing functional groups are created. In order to achieve the goal, 2.4 g of MWCNT were suspended in the mixture of cc. H_2SO_4 (45 cm^3) and fuming HNO_3 (15 cm^3) at 50 ℃ for 24 h. Then, the acid-treated MWCNT was washed to neutral pH and dried over P_2O_5.

The delamination experiments (Li et al., 2005; Liu et al., 2007) were aimed at the preparation of disaggregated LDHs that can be used in layer-by-layer (LBL) experiments (Srivastava & Kotov, 2008), in which layers of LDH and MWCNT were placed on top of each other. They were performed in two ways. In method (D), 0.4–0.5 g of LDH with intercalated DBS was suspended in 100 cm^3 of DMF and stirred for further two days under N_2 atmosphere at room temperature. Whereas in method (E), 5 g of hexamethylenetetramine (hexamine) were dissolved in 160 cm^3 water, then, to 80 cm^3 of this solution, 0.4–0.5 g of CaFe-LDH was added; in the remaining 80 cm^3, 0.4–0.5 g of DBS–LDH was suspended; both mixtures were stirred at 110 ℃ for 24 h, 50 cm^3 of DMF were added and stirring was continued for an additional day.

For the LBL experiments, the used quartz slides were cleaned as follows: immersing into a 1 : 1 volume ratio mixture of 20 mass % HCl and methanol (20 min), rinsing with distilled water, immersing into cc. H_2SO_4 (20 min), rinsing with distilled water, immersing in about 20 M NaOH (24 h), and finally, rinsing with distilled water before use.

In an LBL experiment, the following sequence was used: (i) dipping the quartz slide into suspension (D) or (E) for 20 min, (ii) cautiously rinsing it with distilled water, (iii) dipping the treated quartz slide into a suspension of pristine carbon nanotube (0.3 g nanotube was suspended in 250 cm^3 of distilled water), and (iv) rinsing it with distilled water once again. This sequence was repeated five more times.

The fundamental method for structural characterization was the powder X-ray diffraction. Diffractograms were taken in the 3–60° 2θ region at the 4° min^{-1} scanning rate on a Rigaku Miniflex II (Japan) instrument using the CuK_α radiation (λ = 0.15418 nm).

The composite substances were studied by transmission electron microscopy (TEM, FEI TECNAI $G^2$20 X-TWIN, 200 kV accelerating voltage, USA). Morphologies of the pristine LDH and the composites were studied using a Hitachi (Japan) S-4700 scanning electron microscope (18 kV acceleration voltage) at various magnifications. Elemental maps of the substances were determined with a Röntec (Germany)

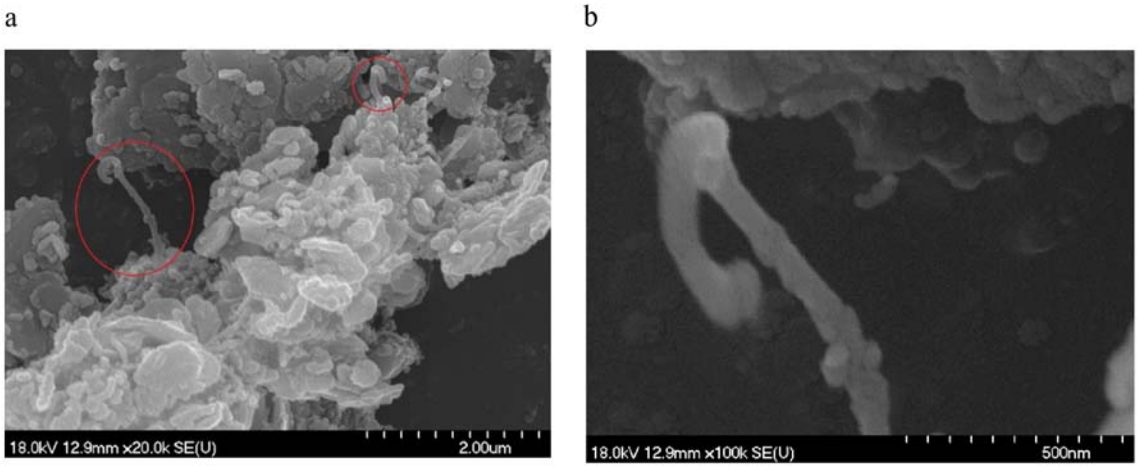

Fig. 2. SEM images of the DBS–pristine MWCNT–CaFe-LDH sample. Magnification: 20000 (a) and 100000 (b) of the encircled part.

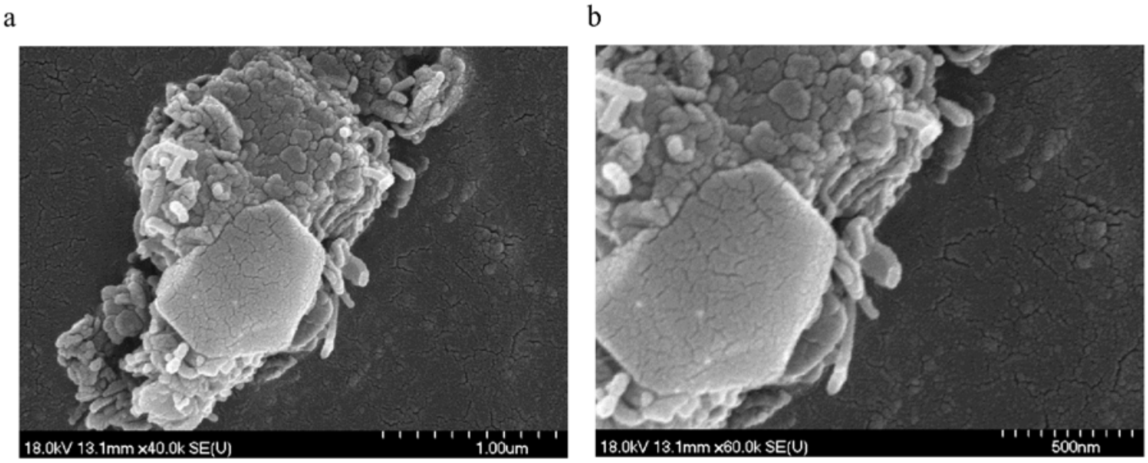

Fig. 3. SEM images of the oxidatively treated MWCNT–CaFe-LDH sample. Magnification: 40000 (a) and 60000 (b).

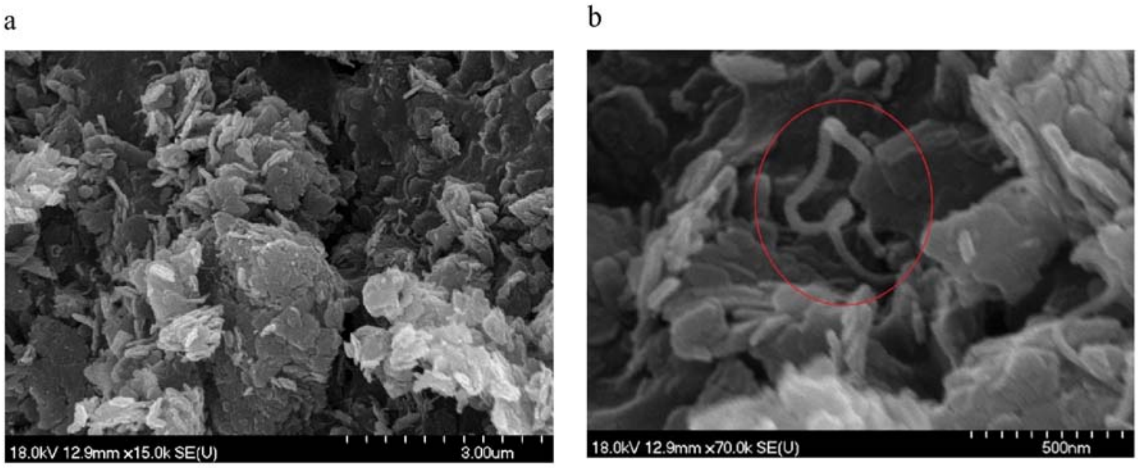

Fig. 4. SEM images of the DBS-oxidatively treated MWCNT–CaFe-LDH sample. Magnification: 15000 (a) and 70000 (b).

QX2 energy dispersive X-ray spectrometer (equipped with a Be window) coupled to the microscope.

Results and discussion

Nanocomposite preparation by the co-precipitation method

The co-precipitation method is the most often used technique to produce LDHs. X-ray traces in Fig. 1 indicate that CaFe-LDHs were really formed. It was also revealed that MWCNT (pristine or treated) did not enter the interlamellar space, i.e. the d(003) values only changed insignificantly in the 0.74–0.77 nm range.

SEM images show the presence of MWCNT (SEM-EDX elemental maps show the presence of carbon in the samples) bundles (judged from the thickness) covered presumably with LDH in the precipitated solid material. These covered MWCNT bundles were only observed when the synthesis mixture contained DBS and pristine MWCNTs (Fig. 2), oxidatively treated MWCNTs (Fig. 3), or DBS and oxidatively treated MWCNTs (Fig. 4).

TEM measurements proved the presence of MWCNT (Fig. 5). Even the multiple walls can be observed. Also, the outer surface of the nanotube is not smooth but covered by a thin layer of LDH.

It can be concluded that although interlayer MWCNT–CaFe-LDH cannot be prepared, MWCNT provides good surface for LDH crystallization only if the MWCNT surface contains enough polar groups (oxidatively treated MWCNT) or if a surfactant promotes the interaction between the apolar MWCNT and the polar LDH.

Nanocomposite preparation by the layer-by-layer method

Obtaining a hierarchically structured nanocomposite consisting of LDH and MWCNTs layers is possible only if the two materials have compatible polarities. Pristine MWCNTs with quite regular apolar structure, vacancies, dislocations, and connected polar

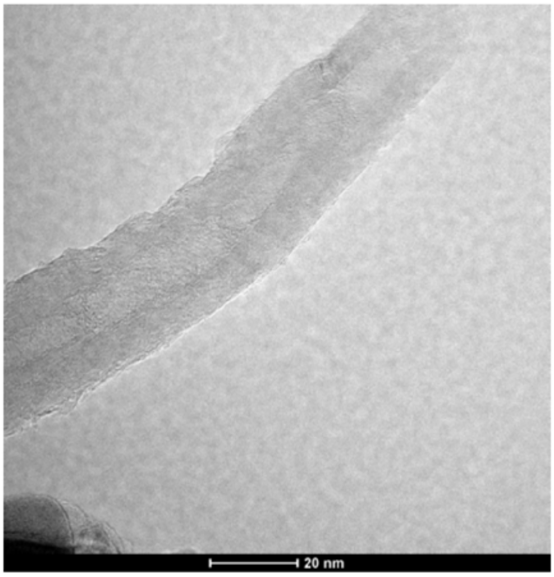

Fig. 5. LDH-covered nanotube from the oxidatively treated MWCNT–CaFe-LDH composite.

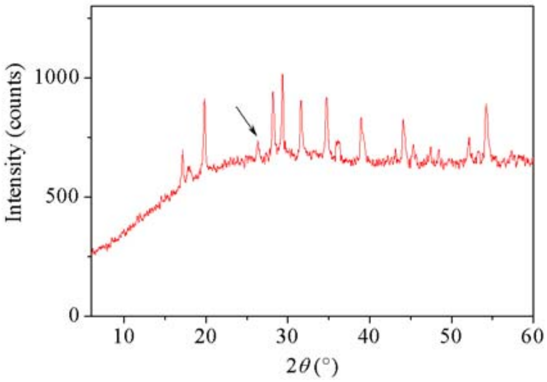

Fig. 7. X-ray diffractogram of the LBL-deposited MWCNT–CaFe-LDH nanocomposite; LDH was delaminated and the reflection typical for MWCNT is marked by an arrow.

groups are rare even if the substance was prepared by the CCVD method. Applying a surface active material like DBS can bridge the polarity gap by adsorption of its apolar part on MWCNT while its ionic part interacts with the delaminated LDH.

Applying the LBL technique, the substances could be layered onto the surface of a thoroughly cleaned quartz slide, as proved by the SEM image in Fig. 6a. Scratching of surface of the treated slide revealed that the layers were really deposited (Fig. 6b).

The X-ray diffractogram in Fig. 7 proves that CaFe-LDH was delaminated and the delaminated layers were deposited (the d(003) reflection is typical for the stacked structure) and indicates the presence of MWCNTs through the weak but observable reflection at 26° 2θ. Nevertheless, it is clear that further optimization of the synthesis conditions is needed.

Conclusions

Preparation of hierarchical MWCNT–CaFe-LDH nanostructures was attempted. It was found that MWCNT bundles provide good surface for LDH deposition when an auxiliary tenside and/or oxidatively treated MWCNTs are used. The layer-by-layer technique was suitable for building a sandwich-like structure by stratifying delaminated LDH and MWCNT in the presence of a tenside.

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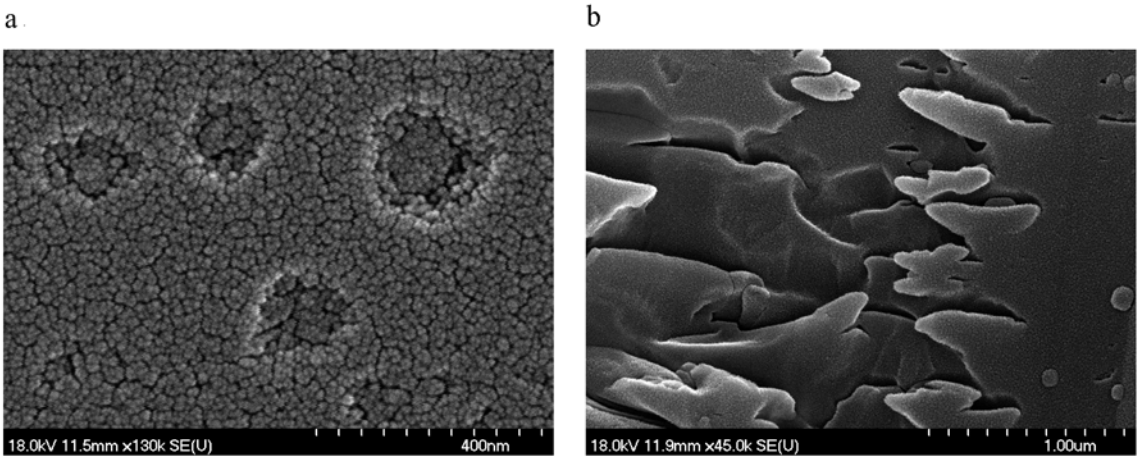

Fig. 6. SEM images of the quartz slide treated by method (E) in order to prepare MWCNT–CaFe-LDH layer-by-layer structure. Top view of the deposited material at a magnification of 130000 (a), and view of the scratched surface of treated slide at the magnification of 45000 (b).

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