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A generic approach for mechano-chemical reactions between carbonnanotubes of different functionalities

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ABSTRACT

Here, we report similar reactions between nanotubes carrying functionalities, namely carbon nanotubes (CNTs) with the acyl chloride/hydroxyl and amine/carboxylic functionalities directly attached to their surfaces, resulting in the formation ofchemically modified graphene products. The reaction is spontaneous and is facilitated by simple grinding of the reactants. The new solid-state reactions have been confirmed using different spectroscopic and electron microscopy techniques.

1. Introduction

Nanoscale materials are attractive due to their unique size, large surface area, chemical and physical properties. Great advancements have been made in the last decade in the synthesis of nanoparticles, which led to new innovative applications in various fields such as catalysis, chemical sensing, photonics, electronic devices and drug delivery [1–8]. Although functionalization has been extensively used to overcome limitations, such as poor solubility, reactivity and processing, by conjugating these particles to different chemical moieties such as drug molecules, polymers or organic molecules, the reactions between differently functionalized nanoparticles have been given very little attention. Especially important, is how do the attributes of these particles reflect on the rate of the reaction and how do the nanoscopic reactivities compare to that of the bulk molecular one. The most remarkable chemical reaction reported between nanoparticles is the dimerization of fullerene molecules inside carbon nanotubes 'peapods' [9,10]. In this type of confinement reaction, the degrees of freedom are restricted to translational motion in one dimension. Encapsulation of the C_{60}s in the CNT peapod structure has been reported to cause a decrease of fullerenes intermolecular distance by 3–4% than in bulk crystals. Structure optimization techniques indicates that the net energy gain associated with the encapsulation of the C_{60}s gives rise to a capillary force with an effective pressure of the order of GPa that will give rise to a strain on the CNT wall. Other than the confinement peapod fullerene/CNT dimerization reaction, no reaction has been reported between nanoparticles of different functionalities. Although an abundance of both top-bottom and bottom-up synthetic strategies have evolved in the last decade for the production of graphene [11–25], none of them considered the solid-state reaction between CNTs of different functionalizations.

We have recently reported the unzipping of MWCNTs via a one-pot room temperature solid-state mechano-chemical reaction between MWCNT–COOH and MWCNT–OH. The reaction involves hydrogen bond mediated proton transfer step that is followed by two elimination steps: water condensation and decarboxylation [26]. To test this type of solid-statedouble eliminations scheme, we here, report two new modifications of mechano-chemical reactions

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of differently functionalized MWCNTs, namely MWCNT–COCl/MWCNT–OH and MWCNT–NH_2/MWCNT–OH reactions, Fig. 1.

Reactions are facilitated by manual grinding of equal weights of the functionalized CNTs as described in our previous report [26]. The two new modifications together with the previously reported one are summarized in equations (1)–(3) [26]

$$\text{MWCNT–COOH} + \text{MWCNT–OH} \rightarrow G + G' + CO_2 + H_2O \quad (1)$$

$$\text{MWCNT–}NH_2 + \text{MWCNT–COOH} \rightarrow G + G' + NH_3 + CO_2 \quad (2)$$

$$\text{MWCNT–COCl} + \text{MWCNT–OH} \rightarrow G + G' + CO_2 + HCl \quad (3)$$

G and G'are the graphene types derived from the two differently functionalized CNTs.

In reaction 2, the unzipping double elimination is mediated by hydrogen-bond formation, followed by proton transfer from the COOH group to the NH_2, double elimination of NH_3 and CO_2, formation of CNTs ion pair and consequent unzipping of CNTs by the heat of the exothermic reaction [26], while the double elimination in reaction 3 proceeds via the condensation of HCl, decarboxylation, CNTs ion pair formation and CNTs unzipping [26]. Each of the above reaction can be considered as a double elimination reaction as summarized in Table.1. Graphene products as well as the double elimination products of the new mechanochemical modifications are confirmed using spectral techniques and electron microscopy ones.

Table 1
Different modifications of the mechanochemical reaction between differently functionalized MWCNTs.

Reaction	Types of elimination
1	Water condensation + decarboxylation
2	Dehydroamination + decarboxylation
3	Dehydrochlorination + decarboxylation

2. Results and discussion

ATR-IR of the solid-state reaction product in the reaction mixture MWCNT–COOH/MWCNT–NH_2 (Fig. 2a), reveals almost complete absence of the strong doublet band at about 3000 cm^{-1}due to the N–H stretching mode as well as absence of broad bands in the region 2500–3000 cm^{-1}due to O–H stretching in the MWCNT–COOH/MWCNT–NH_2 mixture in agreement with water and ammonia condensation reaction. Also, the intensity of the band at 1680 cm^{-1} due to the carbonyl band of the carboxylic group diminishes significantly with appearance of the adsorbed

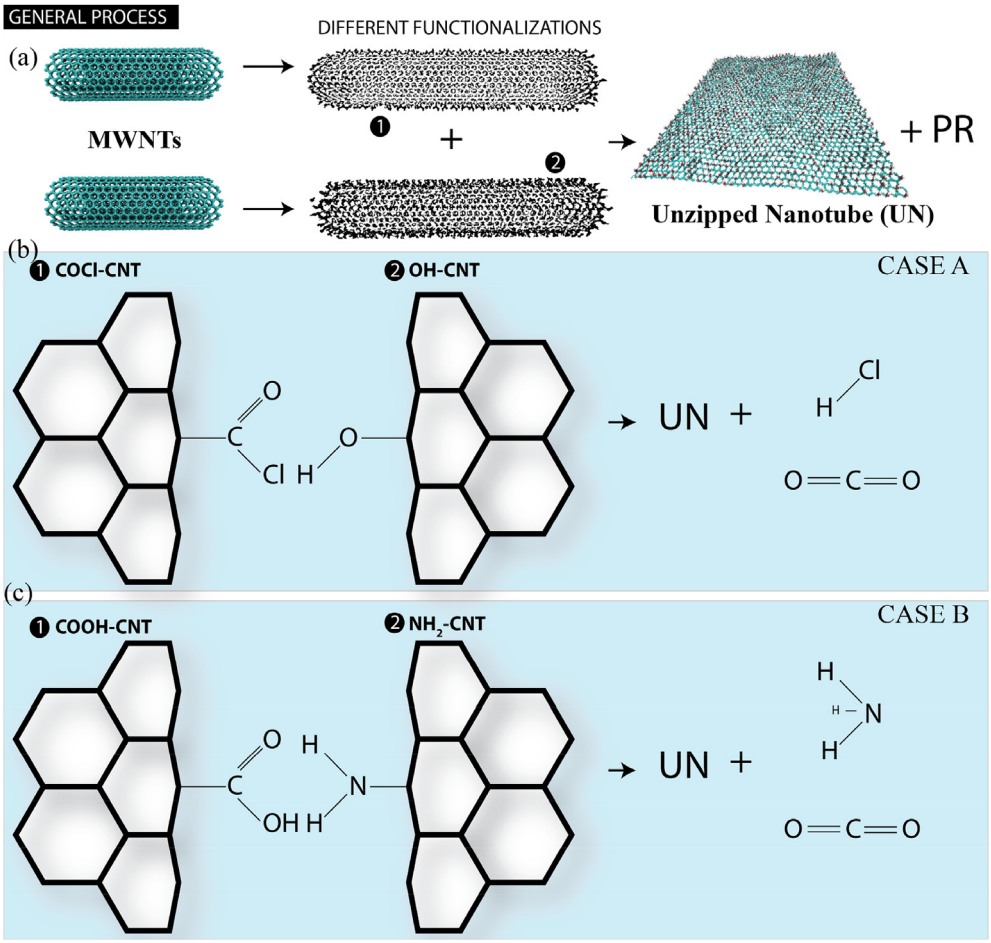

Fig. 1. (**a**) General solid-state unzipping reaction of differently functionalized CNTs. (**b**)Unzipping double elimination reaction between MWCNT–COCl and MWCNT–OH: First elimination leads to the condensation of HCl, which is followed by decarboxylation, formation of CNTs ion pair and consequent unzipping of CNTs by the heat of the exothermic reaction. (**c**) Unzipping double elimination reaction between MWCNT–COOH and MWCNT–NH_2 is mediated by hydrogen-bond formation, followed by proton transfer from COOH to NH_2, formation of the NH_3 and CO_2, formation of CNTs ion pair and consequent unzipping of the CNTs by the heat of the exothermic reaction. (A color version of this figure can be viewed online.)