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Rational recipe for bulk growth of graphene/carbon nanotube hybrids: New insights from *in-situ* characterization on working catalysts

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ABSTRACT

The graphene/carbon nanotube (CNT) hybrids are considered as one of the most advanced nanostructures with intrinsically self-dispersion properties for large-volume applications. However, owing to the limited understanding on the complex growth mechanism and non-linear kinetics, rational design of growth procedures and related multiphase reactors for the production of the hybrids remain great challenges. In this contribution, the *in-situ* monitoring of graphene/CNT hybrid synthesis on layered double oxide bifunctional catalysts was carried out in an online thermogravimetric reactor. The rapid growth of CNTs occurred at the initial 90 s and the slow deposition of graphene was throughout the whole process, becoming the dominant reaction in the second stage. Based on this unique growth behavior, a two-stage growth strategy was proposed to improve the quality of hybrid products. The deposition of amorphous carbon byproduct was significantly suppressed and the quality of the hybrids was significantly enhanced through the two-stage growth process.

1. Introduction

The ubiquitous carbon-based nanomaterials, including zero-dimensional (0D) fullerene, one-dimensional (1D) carbon nanotubes (CNTs), two-dimensional (2D) graphene and other related nanocarbons, have attracted tremendous attention owing to their extraordinary electrical and mechanical properties for a broad field of potential applications [1,2]. However, both 1D CNTs and 2D graphene are inclined to aggregate or stack with each other due to the strong van der Waals forces, which hinder the full exposure of active interfaces for the applications in energy storage and gas sorption [2]. If the 1D CNTs and 2D graphene are rationally integrated into three dimensional (3D) graphene/CNT hybrids, not only the virtues of both graphene and CNTs are inherited, but also effective electronic and thermal conductive 3D networks with an intrinsic dispersion are obtained. Such advanced 3D nanostructures afford unique mechanical, electrical and thermal properties and superior performance in energy storage [3–11], electronic devices [12–14], as well as chemical conversion [12,15,16].

Up to now, myriad approaches have been developed to fabricate this hybrid 3D structure [17], among which the post-synthesis methods were initially explored. Routes including directing mixing [18,19], liquid phase reactions [11,12], casting processes [20], layer-by-layer self-assembly [21–23], evaporation at liquid–air interface [24], hydrothermal fabrication [9,25], electrophoretic deposition [26], and vacuum-assisted filtration [10] have been demonstrated successfully. However, they cannot provide effective connections (*e.g.* the covalent C–C bonding) between graphene and CNTs. This strongly hinders the quality of the products and their further applications. On the contrary, the direct growth method through chemical vapor deposition (CVD) exhibits its advantages in providing the possibility to form the C–C covalent bonding and the variety of anticipated structures [5,8,13,27–31]. Thus, growing CNTs on graphene layers [5,13,14,27–32] and the *in-situ* growth of the hybrids on Cu foil coated with Fe catalyst layers [7,32] were successively reported.

Although these methods are simple and effective to obtain strong graphene-CNT bonding, the growth of CNTs and graphene are quite complex and asynchronous on the bifunctional catalysts [33,34]. In most cases, CNTs preferred to grow on metal catalyst nanoparticles (NPs) and graphene was inclined to deposit on the surface of Cu or metal oxide. Both the bifunctional catalysts and related reactor technologies were highly required for efficient bulk growth of graphene/CNT hybrids. Due to the limited understanding of the growth behavior of hybrids on the bifunctional catalysts, the recipe for large scale production is few touched, although this is the

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first and core step to obtain high quality hybrid samples for the exploration on their bulk application.

In this contribution, the working bifunctional catalyst for graphene/single-walled CNT hybrids (GSHs) was *in-situ* monitored in a thermogravimetric (TG) reactor. The reason to select graphene and single-walled CNTs as the building blocks was attributed from their ubiquitous properties, potentials for bulk applications in high-end products, and their notorious difficulty in good dispersion of each building block. GSHs were widely accepted as the high-end nanocarbon materials for bulk applications in energy storage, adsorption, environmental protection, as well as multifunctional composites [3,4,12,13]. Herein, the growth mechanism of GSH on bifunctional layered double oxide (LDO) catalysts was probed to distinguish the growth rate and duration among CNTs, graphene, and the impurities of amorphous carbon. Based on the growth behavior recorded by the *in-situ* characterization, a two-stage growth strategy was proposed to improve the process efficiency and GSH product quality. Compared with the GSHs fabricated in the routine one-stage way, the GSHs grown in the two-stage method presented a higher purity with fewer amorphous carbons and a larger surface area for their potential applications in energy storage and other fields.

2. Experimental

2.1. Catalyst preparation

The FeMgAl layered double hydroxides (LDHs) were prepared using a facile urea-assisted co-precipitation reaction. Typically, $Fe(NO_3)_3 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and urea were dissolved in 2000 mL deionized water with [urea] = 3.0 mol L^{-1}, n(Fe):n(Mg):n(Al) = 0.4:3:1, and $[Fe^{3+}] + [Mg^{2+}] + [Al^{3+}] = 0.15$ mol L^{-1}. The mixture was then transferred to a 5000 mL glass flask equipped with a reflux condenser. The solution was kept at 100 °C under continuous magnetic stirring for 12.0 h and maintained at 94 °C for 12.0 h without stirring. The FeMgAl LDHs were finally obtained after filtering the as-obtained suspension, washing, and freeze-drying. The $[Mg_{0.69}Al_{0.23}Fe_{0.08}(OH)_2][(CO_3)_{0.155}] \cdot mH_2O$ LDHs were calcined at 900 °C for 0.5 h to obtain FeMgAl layered double oxide (LDO) bifunctional catalysts for GSH growth.

2.2. In-situ monitoring the GSH growth in the TG reactor

In-situ TG investigation of the GSH growth was operated in a TGA/DSC1 STAR^e system. As shown in Fig. 1, 2.0 mg FeMgAl LDO flakes were put into a 70 μL Al_2O_3 crucible, which was inserted into the furnace of the TGA/DSC1 STAR^e system. Then, the furnace was heated to 950 °C with a heating rate of 20 °C min^{-1} under Ar (100 mL min^{-1}) atmosphere. On reaching the reaction temperature, the Ar was switched to the gas mixture of CH_4/Ar with a flow rate of 80/20 mL min^{-1} to start the growth of GSHs. The GSH growth reaction was maintained for 30 min. The mass of working catalysts was recorded by the online mass balance attached with the TG reactor, the reaction heat was *in-situ* collected as the balanced voltage in this system, and the feedstock conversion was determined by the attached on-line mass spectroscopy.

2.3. Bulk growth of GSHs

Bulk CVD growth was carried out to obtain the GSHs on FeMgAl bifunctional LDO catalysts both in a routine way and the coupled two-stage method. A quartz fluidized bed reactor with an inner diameter of 50 mm and a height of 1500 mm was employed. There was a porous sintered quartz plate distributor at the middle of the fluidized bed reactor that served as the support for LDO catalysts and products at the same time. The up-flowing gas mixture entered the reactor from the bottom and then passed through the gas distributor, the fluidized bed unit, and then flowed out from the top of the reactor. During the routine fluidized bed CVD, 10.0 g Fe/Mg/Al LDO catalysts were uniformly fed into the reactor, which was then inserted into a vertical electric tube furnace and heated to 950 °C under Ar atmosphere. The apparent gas velocity was 0.1 m s^{-1} and the methane feed rate was 0.05 $g_{CH4}\ g^{-1}_{LDO}\ min^{-1}$. The growth duration is 15 min. The as-grown samples on the LDO flakes were denoted as one-stage GSHs. While in the two-stage growth procedure, 10.0 g Fe/Mg/Al LDO catalysts were firstly fed into a fluidized bed reactor. CH_4 with a feed rate of 0.15 $g_{CH4}\ g^{-1}_{LDO}\ min^{-1}$ was introduced for 90 s as the first growth period. Then the feed rate of the carbon sources was turned down to 0.03 $g_{CH4}\ g^{-1}_{LDO}\ min^{-1}$ for another 810 s at 950 °C. After that, the fluidized bed reactor was cooled down to room temperature under Ar protection. The as-obtained products were the two-stage GSHs grown on FeMgAl LDO bifunctional catalysts.

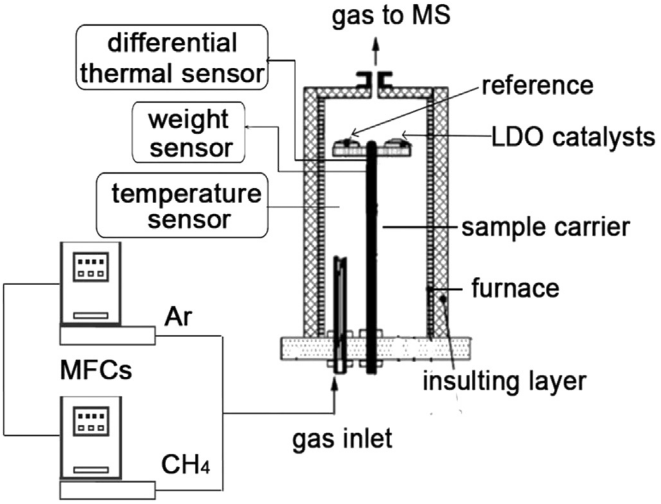

Fig. 1. Schematic illustration of the online TG reactor.

The as-grown raw GSH products were purified with a combined alkali and acid treatment to remove the FeMgAl LDO flakes. Typically, the samples were firstly hydrothermally treated by NaOH solution (15.0 mol L^{-1}) at a temperature of 150 °C for 12.0 h. Subsequently, the as-obtained products were then immersed into HCl solution (3.0 mol L^{-1}) at a temperature of 80 °C for 12.0 h. The as-obtained products were then filtered, washed by deionized water, and freeze-drying, leaving the purified GSH samples (denoted as two-stage GSHs and one-stage GSHs, respectively).

2.4. Characterizations

The morphology of the LDO flakes and the as-grown products were characterized by a JSM 7401F (JEOL Ltd., Tokyo, Japan) scanning electron microscopy (SEM) operated at 3.0 kV, a JEM 2010 (JEOL Ltd, Tokyo, Japan) TEM operated at 120.0 kV and a spherical aberration-corrected Titan3 60–300 (FEI Company) microscope operated at 80.0 kV. The thermogravimetric analysis (TGA) under CO_2 atmosphere was performed using a Mettler Toledo TGA/DSC-1 analyzer. Typically, about 5.0 mg samples were laid into a 70 μL Al_2O_3 crucible, which was inserted into the furnace of the TGA/DSC1 STAR^e system. Then the furnace was heated from 30 to 1400 °C with a heating rate of 20 °C min^{-1} under a mixture of N_2/CO_2 (50/50 mL min^{-1}) atmosphere. The Raman spectra were