



Nanoscale origin and evolution of kinetically induced defects in carbon spheres



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ABSTRACT

Synthesis of carbon nanostructures with controlled defect distribution holds tremendous promise in engineering novel materials for specific device applications and catalysis. Carbon spheres (CS) can be synthesized by controlled thermal pyrolysis of polyethylene (PE) via a series of self-generated pressure reactions. Here, we show that point defect distribution in these CS can be tailored by controlling the kinetics during this synthesis procedure. Using accelerated molecular dynamics, we demonstrate that cooling kinetics during synthesis exercises significant control over the reaction pathways, and consequently, over nucleation and growth of carbon nanostructures. The long-range order of these nanostructures is strongly influenced by the cooling rate. At slower rates <1.4 K/ps, well-ordered carbon onions form with very few defects, while at higher rates >60 K/ps, amorphous carbon with 8–10 membered rings reminiscent of as-quenched carbon melts are seen. In the intermediate regime, the distribution of the defects can be tuned with excellent control. These findings are corroborated by electron microscopy observations of defect formations in synthesized CS. SEM and TEM on CS when cooled from ~973 K (700 °C) to room temperature indicate smooth surface morphologies with a highly defective structure. In contrast, when cooled from ~3073 K (2800 °C), rough surfaces with pronounced 6-membered rings graphitic ordering are observed.

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1. Introduction

Atomic scale defects in carbon nanostructures can significantly alter their physical, chemical, mechanical, magnetic and electronic properties [1–3]. Intrinsic point defects (vacancy-type defects) have a strong influence on the reactivity of carbon nanostructures, making these defective structures as prospective catalysts [4]. Stone-Wales (SW) defects and reconstructed vacancies have been shown to locally change the density of π -electrons and increase reactivity [5]. Point defects such as vacancies tend to reduce the Young's modulus and tensile strength [6]. These defects also strongly influence the electronic properties via local rehybridization of σ - and π -

orbitals in the vicinity of structural defects [7,8]. Apart from point defects, extended line defects in carbon nanostructures have been reported to alter atomic charge distribution as well as electronic spin [9]. Similarly, defects in the graphitic network such as vacancies, interstitials and ad-atoms have local magnetic moments and can give rise to magnetic ordering [10,11]. Evidently, a fundamental understanding of these defects is crucial to design carbon nanostructures with target properties [12]; in particular, their formation dynamics and evolution during the synthesis and processing of carbon nanostructures.

Several types of defects are possible in carbon allotropes (graphene, nanotubes, onions and fullerenes), including edges, grain boundaries, vacancies implanted atoms, and those associated with a change in hybridization state of carbon, e.g., sp^2 to sp^3 [5,9,13]. These defects can be broadly classified as (a) *intrinsic* when the graphitic order is perturbed without any foreign atoms, and (b) *extrinsic* if induced by impurities or dopants [14]. The intrinsic defects may have different dimensionalities; point defects such as

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vacancies or interstitials are zero-dimensional, dislocations are one-dimensional, grain boundaries or stacking faults are two dimensional, whereas inclusions and voids are three-dimensional defects [14]. As aforementioned, each of these defect types strongly influences the physical and electronic properties of nanostructures. A precise control over the location of these defects and their arrangement into ordered and extended structures can allow for design of carbon nanostructures with novel properties [15].

One can clearly envisage several diversified applications of nanocarbon materials by taking advantage of intrinsic and extrinsic defects, which can be induced locally during their synthesis and processing [16,17]. A lot of recent research has therefore been focused on achieving controlled synthesis of defects in graphene and other carbon nanostructures [14,17,18]. For instance, it has been shown that energetic particles such as electrons and ions can be used to induce polymorphic atomic defects in carbon nanostructures as a result of irradiation induced knock-on atom displacements [18,19]. In addition, several chemical methods (e.g., chemical vapor deposition) have been employed to induce intrinsic defects with non-hexagonal bonding geometries [20]. Extrinsic defects can also be incorporated *via* doping agents [14]. In these synthesis methods, it is commonly observed that a high deposition temperature facilitates relaxation towards thermal equilibrium and rapid annealing of defects, while low temperature growth invariably leads to higher amount of defects.

Recently, we introduced a unique route to synthesize carbon nanomaterials using controlled thermal pyrolysis, in which one or more precursors such as polyethylene wastes (PE) are decomposed at elevated temperatures *via* a series of self-generated pressure reactions [21–24]. In this technique, precursors such as PE are heated to high temperatures to attain “supercritical phases” which are allowed to interact in a closed system [21,25]. The thermodynamic and kinetic stabilities of the resultant product phases during the nucleation and growth processes yield new carbon materials (e.g. CS, cobalt-encapsulated carbon nanotubes, metallic core-carbon shell, sausage like carbon bodies, and egg-like CS etc.) in nano-to-micro dimensions [22,24,26–30]. These CS are expected to possess interesting electronic, optical, and other physical properties. For example, these CS have been shown to significantly improve performance when used as lubricants in tribological applications and as anode materials in battery applications [12,24]. We note that the synthesis protocol entails numerous dynamical processes involving a multitude of interfacial reactions, nucleation, and microstructural evolution [22]. Naturally, therefore, the material defect chemistry is a strong function of atomistic transport phenomena across a growing interface, which in turn is influenced by the annealing or cooling dynamics.

Here, we demonstrate using reactive molecular dynamics (MD) simulations that controlling the kinetics of crystallization of amorphous carbon melts (obtained from pyrolysis of PE) allows for systematically altering the defect evolution and distribution in carbon nano-allotropes. The nature and dynamics of crystallization in the ultrafast cooling regime is studied by analyzing the MD simulation trajectories. We track the evolution of graphitic order, intrinsic defects, as well as long-range and short-range order as a function of varying cooling rates. The starting amorphous carbon structures are obtained by high temperature thermal pyrolysis of PE; various dehydrogenated fractions are carefully evaluated to assess the effect of residual hydrogen on the defect chemistry and formation in the final carbon nanostructures. Comparisons to experiments are made where possible. In particular, experiments are used to understand the effect of cooling on the formation of microstructural defects whereas atomistic simulations are used to understand the evolution of intrinsic and topological defects during

the synthesis of carbon structures from polyethylene wastes. Our study demonstrates that new families of nanocarbon allotropes with controlled defect distribution can be formed from amorphous carbon by kinetically tuning the crystallization dynamics.

2. Methods

2.1. Experiments

2.1.1. Synthesis of carbon spheres (CS)

The CS were synthesized by the controlled thermal decomposition of either organic compound such as trashed polyethylene terephthalate [31], polyethylene bags [24] or mesitylene (C_9H_{12}) [26]. The reactor is specially designed using Haynes 230 alloy to hold pressure up to 2000 psi and temperature could be as high as $\geq \sim 1073$ K (≥ 800 °C). To release excess overpressure built in autoclave, the pressure release valve was also connected. Since the cracking/dissociation of hydrocarbon reaction occurs above ~ 773 K (500 °C) [32], most of such reactions are carried out at ~ 973 K (700 °C) with a heating rate of 20 °C/min. The dissociation of hydrocarbon occurs in a short time and thus the reactor was held at ~ 973 K (700 °C) for 5–10 min, which usually generates pressure of less than 1000 psi at elevated temperature. Thereafter, the heated reactor was cooled naturally to room temperature. The procedure was repeated by synthesizing at ~ 3073 K (2800 °C) and subsequently cooling the sample to room temperature. The typical yield of dry, CS was 40–45 wt. %. TEM characterization was performed on the Argonne Aberration-Corrected TEM (ACAT) operated at 80 kV to minimize electron beam-damage to the sample [33].

2.2. Computational details

2.2.1. Simulation set-up

In the first step, we carried out atomistic simulations of thermal decomposition of PE chains by using second-generation reactive empirical bond order (REBO) potential [34,35]. This potential allows for dynamic breakage and formation of chemical bonds in a variety of hydrocarbons that are likely to form during the thermal decomposition and quenching of hydrocarbon precursors. The decomposition of PE was studied by randomly placing 28 chains of PE consisting of 100 monomer (100-mer) units in a simulation cell with dimensions (80 Å × 80 Å × 80 Å). The ends of each individual PE chain were terminated with hydrogen atoms. The initial equilibration of the PE chains was carried out at room temperature (~ 300 K) by performing simulations in a canonical ensemble for 500 ps with a 1 fs time-step [36].

Thermal decomposition of PE was carried out *via* temperature accelerated reactive molecular dynamics (TARMD) runs in LAMMPS by simulating the systems at temperatures as high as 7000 K [37]. Our focus here was to completely decompose the polyethylene (PE) and remove the free hydrogen atoms within the MD time scales. Hence, 7000 K was chosen as a reference temperature as it is sufficiently higher than the melting point of PE and carbon end product. Thus, TARMD technique enables us to explore the degradation mechanism of polymer chains within the time scales accessible to MD simulations. In a typical chemical reaction at elevated temperatures, the hydrogen atoms from the dissociated hydrocarbons escape the system through a free surface or a gas–liquid interface [22,24]. In order to emulate experimental conditions of gas–liquid phase separation and decomposition of the polymer in TARMD simulations, it is very important to have an accurate and efficient hydrogen removal scheme. Experimentally, the carbon–hydrogen (C–H) and hydrogen–hydrogen (H–H) bond lengths are reported to be 1.09 Å and 0.74 Å, respectively; these bond lengths are accurately reproduced by the REBO potential

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