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Synthesis and characterization of carbon nanostructures by evaporating pure graphite and carbon black in detonation-gas arc discharge

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ABSTRACT

Arc discharge experiments combined with explosive detonation have been carried out to probe the transformation of pure graphite and carbon black evaporated in detonation gas. Under respective conditions, different kinds of carbon nanostructures have been synthesized including few-layer graphene (FLG) nanosheets, polyhedral graphite particles (PGPs), carbonaceous monocrystals and graphene oxide (GO). The evaporation of graphite facilitates the formation of FLG and PGPs, which exhibits competitive growth according to the pressure of detonation gas. By evaporating carbon black, a considerable amount of high-crystalline GO with low oxygen concentration are acquired. The morphology, crystal structures, Raman spectroscopic fingerprints and chemical compositions of these products are investigated by the characterizations of transmission electron microscopy (TEM), high-resolution TEM, Raman spectra and X-ray photoelectron spectroscopy. The formation mechanisms of such carbon nanostructures in arc evaporation are discussed according to the chemical nature and pressure of detonation gas.

1. Introduction

Carbon atoms are known to exist in three states corresponding to sp, sp^2, and sp^3-hybridization of their valence orbitals. In 1997, Heimann et al. proposed a classic ternary "phase" diagram of carbon allotropes for the first time, clearly pointing out the correlations and transformation routes of carbon allotropes with varying ratios of hybridizations of sp, sp^2, and sp^3 [1]. For years, people are fascinated by the mutual transformation between sp-carbon (carbyne), sp^2-carbon (graphite) and sp^3-carbon (diamond) under various experimental conditions. For example, the conversion from sp^2- to sp^3-carbon under instantaneously high temperature and high pressure is well known as a main method to artificially produce ultrafine diamond (UFD) using sp^2-carbon as starting carbon source, which is called detonation method [2,3]. Detonation gas is usually generated by the detonation of pure or composite CHNO explosives with negative oxygen balance. The chemical reaction of explosive detonation is very fast and complex, producing free atoms of C, H, N, and O with dangling bonds. Due to deficient oxygen atoms, these atoms tend to combine as N_2, H_2O, CO, CO_2 and a small amount of free carbon [C]. Hence the detonation gas is a kind of gas mixture with chemical reducibility. The carbon transformation and yield of UFD are also associated with the types and ratios of explosives, which result in different chemical atmospheres and pressures for the formation of UFD. Regardless of pressure, the pure effect of chemical compositions of such complex gas mixtures on the hybridization and structural transformation of carbon allotropes under high temperature and negative pressure was still not clear.

Arc discharge, also known as arc plasma, is one of the most efficient and versatile tool of fabrication of various carbon nanostructures [4–8]. In contrast to top-down synthesis, arc discharge is ascribed to bottom-up method due to the condensation and growth of carbon vapor consisting of small clusters with various atomicities when the anode was evaporating during discharge. Factors influencing the preparation of this method include arc current/gap voltage, the type and ratio of buffer gas, external fields and catalysts. Among them, the type and ratio of buffer gas plays decisive role in the formation and property of end-products since arc plasma is enhanced by the ionization of buffer gas. Take hydrogen for example, the presence of hydrogen in arc discharge not only terminates the dangling carbon bonds with hydrogen and prevents the formation of closed structures [6,9], but raise the temperature of arc torch since it is prone to dissociate [10,11].

Such complex gas mixtures influence the end-products of arc discharge because massive detonated atoms will combine with a great quantity of metastable carbon radicals (C_1, C_2, C_3, C_4…) evaporated by discharge. How to evaporate and condense carbon vapor in such complex buffer gas have not been reported previously and it motivated us to investigate these. To combine arc discharge and detonation method, the transformation of carbon allotropes under high temperature and negative pressure can be probed. Therefore, we designed a series of novel experiments to investigate the condensation and formation of carbon allotropes in detonation-gas arc discharge. Our trials can figure

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out the possible routes of pure graphite and carbon black to transform and recondense in detonation-gas arc discharge with high temperature and negative pressure.

2. Materials and methods

Detonation gas was produced using an explosive device including explosive, detonator, a hermetic high-strength steel vessel and trigger box, which is illustrated in Fig. 1(a). Fig. 1(b) and (c) shows the explosive chamber before and after detonation, respectively. The charge is a mixture of 60 wt.% TNT (trinitrotoluene, $C_6H_2(NO_2)_3CH_3$) and 40 wt.% RDX (hexogen, $C_3H_6N_6O_6$) with a total mass of 50 g. The whole system was maintained under high vacuum (~10^{-2} Pa) before explosion to ensure the acquisition of pure detonation gas for the following discharge experiments. To avoid the interference of impurities and dust generated in the detonation, the discharge experiments were carried out after a few seconds when the explosion was done. Raw soot samples were synthesized in a direct-current arc discharge device and collected from the inner wall of discharge chamber. The pressures of detonation gas for discharge were 20, 50, 70, and 90 kPa. Rod-shaped pure graphite and carbon black anodes of 5 mm in diameter and a rod-shaped pure graphite cathode of 15 mm in diameter were customized to serve as the electrodes. The arc current and gap voltage were maintained at 120 A and 20 V, respectively. The electrode gap was kept constant (~1.5 mm) by mechanically adjusting the anode.

All samples were characterized by employing transmission electron microscopy (TEM, JEOL-200CX) and high-resolution transmission electron microscopy (HRTEM, JEM-2100). The acceleration voltages of TEM and HRTEM are 120 and 200 kV, respectively. The sizes of selected-area apertures are 500 and 200 nm in our experiments. Raman spectra were recorded with a HR-800 laser confocal micro-Raman spectrometer using laser excitation wavelength of 514.5 nm. X-ray photoelectron spectroscopy (XPS) was collected from the instrument using monochromatic Al irradiation source (Kratos Axis Ultra DLD).

3. Results and discussion

3.1. TEM and HRTEM analyses

Fig. 2 exhibits the typical TEM images of carbon nanostructures prepared under respective pressure conditions. In Fig. 2(a), few-layer graphene (FLG) nanosheets with lengths of 100–200 nm are main

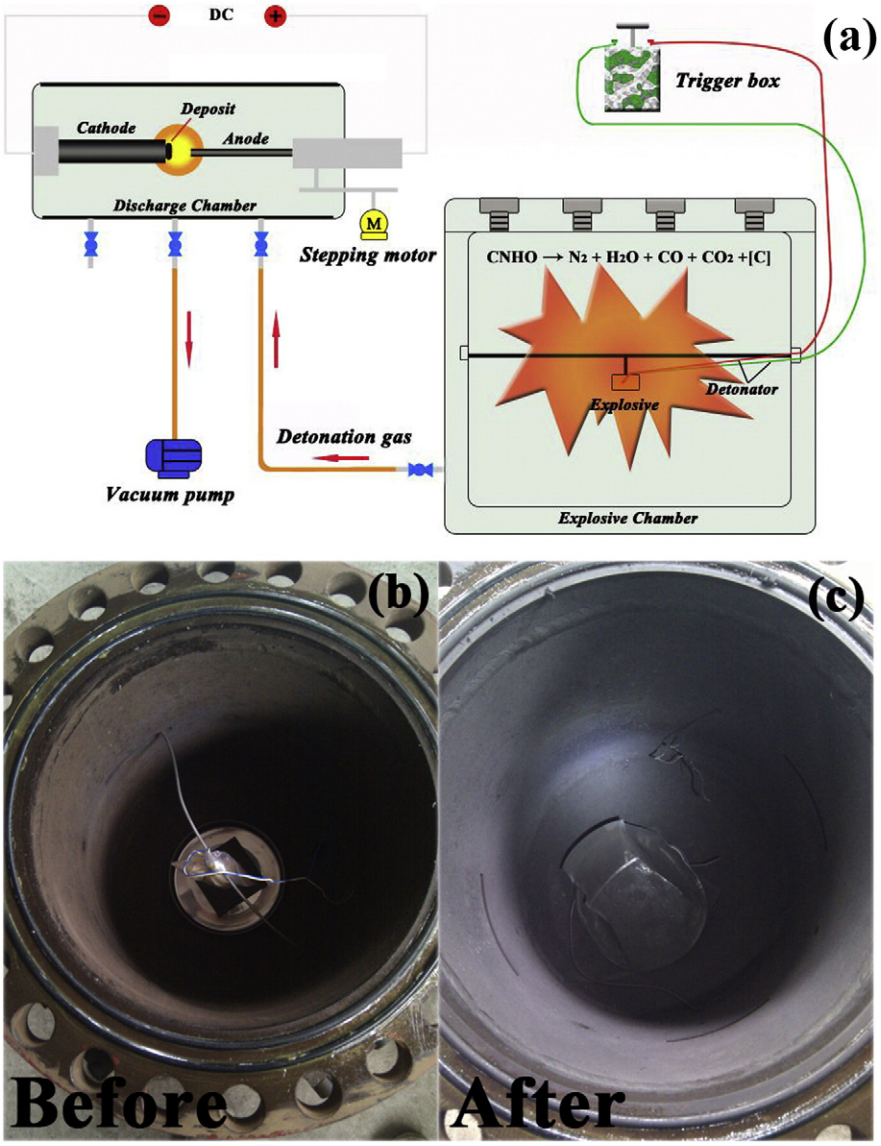

Fig. 1. (a) Schematic of arc-discharge apparatus combined with explosive device. (b, c) Images of explosive chamber before (b) and after (c) detonation.