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Synthesis of uniform monolayer graphene on re-solidified copper from waste chicken fat by low pressure chemical vapor deposition

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ABSTRACT

A technology for converting waste materials to high quality large-area monolayer graphene film can be significant and thereby obtaining high value-added product. Here, we revealed the transformation of waste chicken fat into uniform monolayer graphene film on re-solidified Cu by a low pressure chemical vapor deposition (LPCVD) technique. The evolve gas analyzer-gas chromatography–mass spectrometry (EGA-GC–MS) analysis of chicken fat oil showed that the free fatty acid in chicken oil decomposed into a short hydrocarbon chains which makes it favorable to use as a carbon precursor for graphene synthesis. Growth of uniform monolayer graphene film on the re-solidified Cu was confirmed by Raman mapping, where 2D to G peak intensity ratio (I_{2D}/I_G) is 3.0 at most of the area. Thus, the use of waste from poultry industry as a carbon source instead of commonly used hydrocarbon gas sources for graphene synthesis can be an approach for green nanotechnology.

1. Introduction

Chemical vapor deposition (CVD) technique has been significantly explored owning to the possibility of synthesizing high quality graphene film in large-area [1–3]. Recent studies also demonstrate control synthesis of bi-layer stacks and large single crystal domains on the metal catalytic substrate [4–10]. The synthesis of graphene film has been achieved by low and atmospheric pressure CVD techniques using methane as the primary carbon source [2,11–14]. Meanwhile, liquid and solid carbon sources, such as ethanol, benzene, camphor, poly (methyl methacrylate) (PMMA) and sucrose have been investigated for graphene synthesis as an alternative to gaseous sources, taking into account the advantages of simpler and controllable CVD process [15–19]. As in line with green nanotechnology concept, solid waste carbon precursor such as camphor, waste plastics, coffee ground, insects, and food waste are gaining more attention in graphene synthesis recently [19–22]. These materials are highly available and can be directly placed in the CVD chamber without any external carbon source supply system. However, considering the possibility of high quality graphene synthesis by a low pressure CVD (LPCVD) technique, the choice of solid or liquid carbon precursor is very much critical as the vapor pressure of precursor significantly influence the carbon flux.

Thus, we explored the feasibility of using waste from poultry processing industries, namely waste chicken fat (WCF) to synthesize high quality graphene in a LPCVD process. WCF is a free fatty acid (FFA) rich resources, thereby making them as a good option for alternative and promising carbon source. Recent reports show that WCF is composed of oleic ($C_{18}H_{34}O_2$), palmitic ($C_{16}H_{32}O_2$), and linoleic ($C_{18}H_{32}O_2$) acids [23–25]. High purity

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and controllable vapor pressure of WCF widens its usage either in atmospheric pressure CVD (APCVD) or LPCVD. Furthermore, the high consumption of chicken nowadays indicates the high availability of waste discarded by the chicken processing industry as compared to other poultry. With poor current management practices of food waste like incineration, which resulted in secondary pollution throughout greenhouse gas emissions, the utilization of WCF into high value added product would not only reduce the amount of solid waste, but it is also contribute to conserve natural resources, and save energy and hence fuel [26,27]. In this regard, we demonstrate for the first time, the direct utilization of WCF without any special treatment to synthesis high quality graphene by the LPCVD method. The high quality and excellent transparency of homogeneous monolayer graphene were confirmed by Raman, AFM, SEM and UV–vis analysis, respectively. Less wrinkles formation in the as-synthesized monolayer graphene on a re-solidified smother Cu surface was achieved, enabling fabrication of transparent electrode with low sheet resistance.

2. Experimental details

Graphene films were grown on 20 μm thickness Cu substrate (Nilaco Corp., purity 99.9%) using LPCVD method. The Cu substrate was annealed in an enclosed tube at 1100 °C for 60 min with flow of 100 sccm (standard cubic centimeter per minute) of H_2 gas. Next, Cu substrate was loaded into the quartz tube of length 90 cm and diameter of 5 cm. The chicken oil, which was used as a carbon precursor was extracted from chicken fat and skin by a dry rendering process (Fig. 1a and b). In this process, the fat and skin were heated to 200 °C to separate liquid oil from solid [24]. Magnetic boat containing chicken oil was placed near the opening of the inlet. Fig. 1c shows the schematic diagram of LPCVD used in the graphene growth. The system was pumped down to a vacuum pressure of 2 Pa for 10 min, and then heated to 1080 °C within 120 min with 100 sccm of pure H_2 gas. Then, the mixture of Ar and H_2 gas with a molar ratio of 98:2 sccm were introduced into the LPCVD system and the magnetic boat containing chicken oil was brought into the zone and placed at 5 cm away from the zone for the graphene growth at 1080 °C under pressure of 150 Pa for 60 min. After the completion of the synthesis, the furnace was allowed to cool down to room temperature.

In order to transfer graphene, PMMA was spin coated at 3000 rpm for 1 min followed by baking at 180 °C for 1 min. Next, the transfer was carried out by electrochemical delamination to avoid contaminations. 0.25 M sodium hydroxide (NaOH) was used as an electrolyte at 10 V and 400 mA. The PMMA/graphene/Cu was dipped into a NaOH aqueous solution and used as a cathode of an electrolysis cell with a constant current supply. At the cathode, a water reduction reaction took place to produce H_2 bubbles. The PMMA/graphene layer was observed to be detached from the Cu substrate after a few seconds as a result of the formation of a huge number of H_2 bubbles at the interface between the graphene and Cu substrate. After cleaning with pure water, the floating PMMA/graphene layer was transferred to the target substrate. Finally, the PMMA was removed by treatment of hot acetone (80 °C).

The characterization of WCF, bare and re-solidified Cu, as-synthesized and transferred graphene samples involved evolve gas analyzer-gas chromatography-mass spectrometry (EGA-GC–MS) by Shimadzu GCMS-QP2010, electron back scattered diffraction (EBSD) by JEOL JSM-7001FF field emission SEM equipped with an EBSD detector, atomic force microscopy (AFM) by SPM-5200 scanning probe microscopy, optical microscopy (VHX-500 digital microscope), Raman spectroscopy (NRS 3300 laser Raman spectrometer with a laser excitation wavelength of 532.08 nm), TEM (JEOL JEM 2100, operated at 200 kV), UV–vis spectroscopy (ASCO V–670 K spectrophotometer), and sheet resistance measurement by four probe (T–70 V/RG-7C of Napson Corporation).

3. Results and discussion

In the present work, the growth of uniform monolayer graphene from WCF on Cu substrate by LPCVD is demonstrated. WCF is an abundant waste material that was produced every day in the world and the utilization of this waste material as a carbon precursor for graphene synthesis stand unique. It is sure to have a great impact in recycling process and waste management. To investigate the suitability of WCF in the synthesis of graphene, EGA with GC–MS analysis were done to determine its chemical composition. The chicken oil is examined by EGA-GC–MS to investigate the content of carbon evolve during the thermal decompositions. Fig. 2a shows the EGA of evolve products at different temperatures. EGA spectrum shows the decomposition of carbon source occurred mainly around 400 and 550 °C with retention time of 17.5 and 25.0 min, respectively. Fig. 2b and c show average pyrolysis GC–MS spectra, as complying to further analyze the major product evolve during the decomposition process. At a decomposition temperature of 400 °C, linear carbon chain fragmented with 3, 4 and 5 carbon atoms are observed in abundance, whereas at 550 °C, the accumulated triglycerides which accidentally moved to MS detector was found. Considering the EGA-GC–MS analysis, the WCF was heated around 400 °C in the CVD synthesis process. This will produce abundant of low molecular weight carbon molecules for favorable graphene growth. Previously, Suriani et al. have demonstrated carbon nanotubes (CNTs) synthesis using WCF precursor by heating at 470 °C [25]. In contrast to previous work, we heated the precursor at a lower temperature taking account of the gas chromatography analysis, which enable us to extract smaller carbon chains. The low molecular weight aliphatic carbon can easily dehydrogenated on Cu catalyst substrate, which can be significant to achieve homogeneous uniform monolayer graphene growth.

The metal substrate use for synthesis of graphene also plays important role in monolayer graphene formation [28]. In this experiment, the polycrystalline Cu substrate was used as a catalyst. Fig. 3a–c shows the structural characterization of bare Cu substrate. The surface of the bare Cu substrate appears to be very rough as observed in the optical image (Fig. 3a). AFM analysis in Fig. 3b shows that the bare Cu has a high surface roughness with root mean square (RMS) value of 300 nm. EBSD measurement was performed to investigate the plane of Cu substrate. EBSD result (Fig. 3c) shows that bare Cu substrate consists of different orientations of grain on the surface; mostly covered by Cu (100) and Cu (110) planes. The grain on the surface is associated with the processing steps as well as the difference in the purity of Cu. In this experiment, the Cu substrate was re-solidified at 1100 °C for 60 min under the flow of H_2 (100 sccm) to expand the grain size, remove the native oxide layer and smoothen the surface. The evolution of randomly curve grain boundary is shown in Fig. 3d–f. Optical microscopy image shows that the re-solidified Cu substrate has large grain size (more than 400 μm) with a smooth surface. AFM results in Fig. 3e proved the smoothness of Cu surface as the RMS value is very low (∼30 nm). Again, EBSD result shows that the re-solidified Cu substrate consists only Cu (111) plane with minimum amount of Cu (100) plane (Fig. 3f). The EBSD result is supported by XRD pattern which showed the presence of Cu (111) (as shown in inset of Fig. 3f). In LPCVD, previous studies by Robert MJ and Ivan V et al. show that graphene growth is a substrate mediated process, and the shapes of the resulting graphene domains are determined by the symmetry of the underlying facet [28,29]. Cu (111) and Cu (100) play a crucial role in the coalescence of graphene domains and completion of the self-limiting process to produce monolayer