DROPLET-BASED 3D GRAPHENE STRUCTURE SYNTHESIS

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ABSTRACT

In this study, we presented a droplet-based microfluidic system for synthesizing three-dimensional (3D) graphene structure, called graphene popcorn. The droplets that were obtained by varying the flow rates and the concentration of graphene oxide (GO) solution were incubated in the furnace for rapid evaporation, resulting in the reduction of the GO as well as the aggregation of GO to form the graphene popcorn. The size of the 3D graphene popcorn could be controlled by the flow rate of the oil phase, and the aggregation degree was tuned by the GO concentration.

KEYWORDS

Graphene, Graphene oxide, Graphene popcorn, Droplet, Capillary compression

INTRODUCTION

In recent years, graphene, an one-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in honeycomb crystal lattice, has attracted huge attention due to its extraordinary physical, chemical, and mechanical properties [1]. Due to these characteristics, graphene has been widely investigated to be applied for electronics, energy devices, and biosensors. Although the use of the two-dimensional (2D) graphene structure is focused so far, the three-dimensional graphene also can find its unique application fields by utilizing the excellent properties such as high compression and aggregation resistance, high surface area and the pore structure. Thus, the assembly method for converting the 2D graphene into 3D structure is of importance, and several approached were proposed, including layer-by-layer assembly, vacuum centrifugation, and template-directed chemical vapor deposition/encapsulation [2,3]. Recently, an aerosol assisted self-assembly method was reported by Luo et al. for generating 3D graphene structure to be applied for energy storage and conversion devices [4]. However, the previous methodology lacks the precise controllability in size and morphology of the 3D structure. The droplets based on the microfluidic device have demonstrated the high uniformity, size controllability, fusion/division of droplets, and fast chemical reaction rate in the droplets. Herein, we utilized the advantages of the microfluidic droplet generator to produce 3D graphene structure.

EXPERIMENT

A microfluidic droplet generator was fabricated by using soft lithography and operated by a syringe pump to inject a GO solution and a surfactant/oil solution. The design of the chip is shown in Fig. 1. The chip consists of three inlet ports, an outlet port, a cross-junction region, and a passive mixer region.

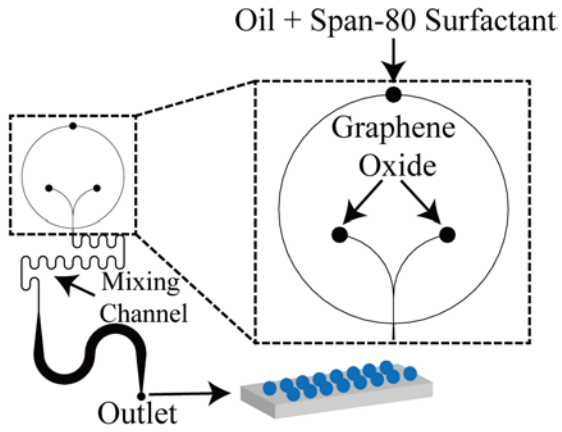

Figure 1: Schematic illustrations of the droplet generator for synthesizing droplets containing a GO solution.

Uniform droplets could be generated with an aqueous graphene oxide (GO) solution and an oil phase solution. A water-dispersible and single-layered GO solution was prepared by a modified Hummers method and n-hexadecane was used as an oil phase solution. 2 mg/ml, 5 mg/ml, and 10 mg/ml concentration of GO solutions were encapsulated in the droplets (0.18 nL) with background of continuous oil phase (Hexadecane with 2 wt% Span-80 surfactant). The flow rate of a GO solution was fixed at 1.0 μl/min, and that of an oil phase was changed at 10, 25, and 50 μl/min, thereby producing different size of droplets (70, 64, 48 μm). The droplets were collected on a silicon wafer (1.5 × 1.5 cm) and the wafer was loaded in the furnace at 800 ^{o}C with hydrogen gas. The liquid phase was rapidly evaporated that resulted in the aggregation of a 2D GO to form 3D structure. At the same time, the GO was reduced under the conditions of high temperature and hydrogen gas flow. The produced graphene popcorns were

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detached from the silicon wafer by ultra-sonication process and purified by centrifugation for SEM analysis.

RESULTS AND DISCUSSION

The nano-sized GO sheets were synthesized by the Hummers method as shown in the left image of Fig. 2(a). The GO sheets in the droplets were aggregated by the capillary compression process during the evaporation in the furnace (right image of Fig. 2(a)). The formed 3D graphene structure displays a spherical shape with packed graphene sheets similar to the popcorn. In Figure 2b, X-ray photoelectron spectroscopy (XPS) data show that the GO sheets were almost completely reduced under the conditions of 800 ^{o}C and hydrogen gas flow. The peaks of carboxyl and hydroxyl groups were suppressed, while the sp^2 carbon peak was shown as a majority in the reduced graphene popcorn.

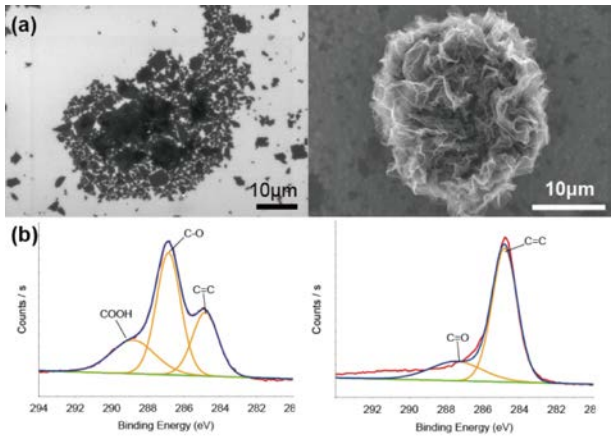

Figure 2: (a) SEM images of a single-layered GO and an aggregated graphene popcorn. (b) XPS spectra of the GO and the reduced graphene popcorn.

We loaded different concentration of a GO solution (2, 5 and 10 mg/ml) to investigate the change of morphology. As the GO concentration increased, the degree of aggregation was enhanced, so the more densely packed graphene popcorn was generated (Fig. 3d-3f). However, the size of them was not significantly affected by the GO concentration (Fig. 3). The average diameter was 36.39 (± 6.42) μm, 39.19 (± 5.34) μm, 32.478 (± 5.37) μm when the used GO concentration was 2, 5, 10 mg/ml, respectively (Fig. 3g).

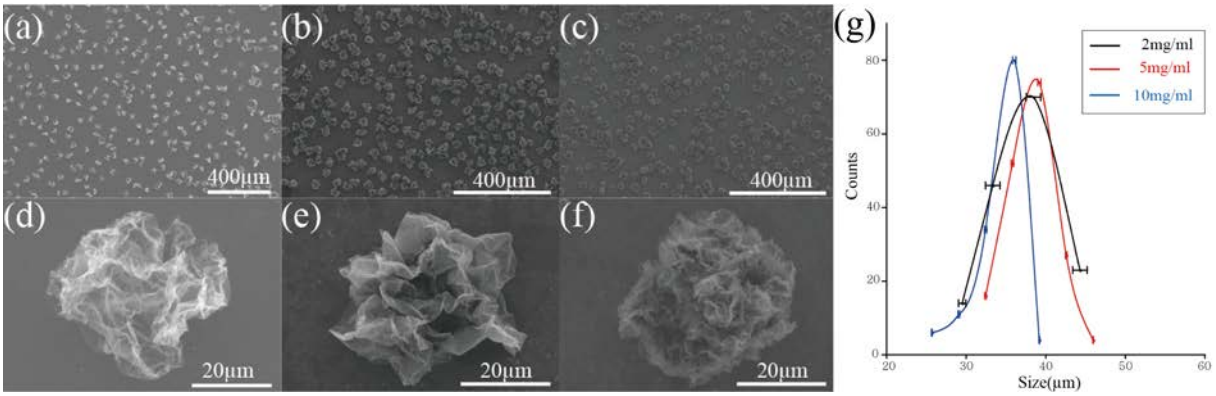

Figure 3: SEM images of graphene popcorns with variation of the GO concentration: (a) 2 mg/ml, (b) 5 mg/ml, (c) 10 mg/ml. (d-f) Enlarged images of (a-c). (g) The size distribution of graphene popcorns.

These results mean that if the 3D graphene with higher surface is required, the more concentrated GO solution should be used. However, the size of graphene popcorn was independent of the GO concentration. It seems that the size controllability was dependent on the droplet size, not the graphene concentration. Thus, we hypothesized that we could tune the size of the graphene popcorn by controlling the droplet size. We changed the flow rate of an oil solution with 10 μl/min, 25 μl/min and 50 μl/min, while the flow rate of the GO solution was set to 1.0 μl/min. The used GO concentration was 10 mg/ml in all the cases. As the flow rate of an oil solution was increased, the diameter of the droplets was decreased to 70, 64, 48 μm. As a result, the size of the synthesized graphene popcorn was gradually reduced as the flow rate was increased (Fig. 4). The average diameter of graphene popcorns was 32.48 (± 5.37) μm, 22.78 (± 2.83) μm, 17.845 (± 2.41) μm at the flow rate of 10 μl/min, 25 μl/min and 50 μl/min, respectively.

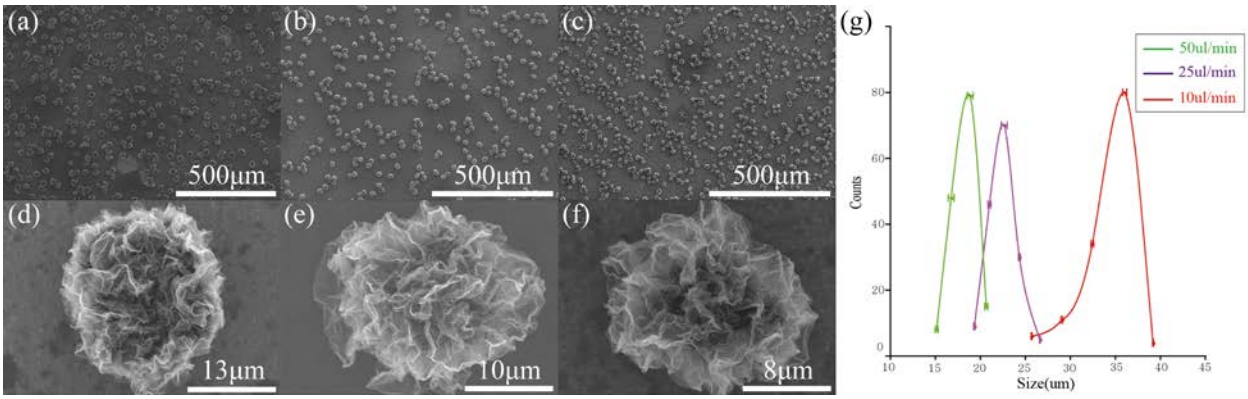

Figure 4: SEM images of graphene popcorns with variation of the flow rate of an oil phase: (a) 10 μl/min, (b) 25 μl/min, (c) 50 μl/min. (d-f) Enlarged images of (a-c). (g) The size distribution of graphene popcorns.

The resultant 3D graphene on the silicon wafer was recovered by ultra-sonication process for 20 min. Then, the graphene popcorns was purified and concentrated by centrifugation. The 3D graphene popcorn was successfully obtained without structure deformation (Fig. 5).

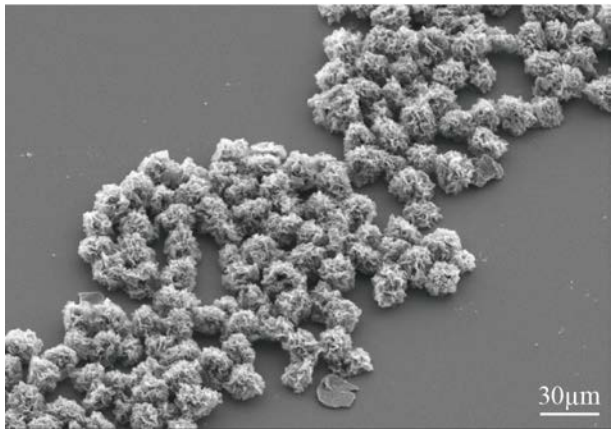

Figure 5: SEM image of graphene popcorns after collecting from the silicon wafer.

CONCLUSION

We have demonstrated the synthesis of the 3D graphene structure, called graphene popcorn, by using a microfluidic droplet generator and capillary compression during thermal evaporation. The size and morphology of the 3D graphene structure was controlled by the flow rate of the oil solution and the concentration of the GO solution. This novel structure of graphene could be applied in the fields of polymer composites, biosensors, and catalyst supports.

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