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3D-PRINTING GRAPHENE OXIDIZE BASED ON DIRECTIONAL FREEZING

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Abstract

This paper aims to provide a new process that is based on micro-dispensing and directional freezing to fabricate macro and micro controllable 3D graphene aerogel. In the first section, a design model of the proposed system to print 3D graphene oxide is presented, and the configurations are discussed in detail. The presented new method is contrasted to other few graphene 3D printing process. A process planning is provided includes the complete fabrication process and printing process. The physics mechanism behind the process is illustrated. A list of 2.5D and 3D printed samples are shown. Graphene Oxide solution is an easy to print material for micro-dispensing device, we successfully printed GO solutions in a stable and reliable way. Our freezing based 3D printing process matches well with freeze drying technology, which together composes the key step for fabricating truly 3D graphene aerogel.

1. Introduction

Graphene aerogel, large-scale assembly of two-dimensional (2D) graphene into three-dimensional (3D) bulk, have been extensively investigated in order to explore the macroscopic applications of graphene, such as energy storage, thermal insulation, sensing, electronic, biomedical and functional composite (Ye et al., 2013, Menzel et al., 2015, Xu et al., 2015, Leigh et al., 2012, Cong et al., 2013, Wicklein et al., 2015, Jakus et al., 2015, Maiti et al., 2014). However, tailored macro-architecture of graphene aerogel for specific application via controllable and scalable assembly method remains a significant challenge. In order to fully exploit the exotic physicochemical properties of 2D graphene material and explore its broader range of macroscopic applications, there is an urgent need to develop a new 3D printing technique that can print pure and continuous graphene aerogel with truly 3D architecture.

3D printing is a disruptive manufacturing technology that can selectively deposit material in 3D space to form complex object. This unique property makes 3D printing the best candidate for fabricating engineered graphene aerogel with complex structures. However, due to the universal challenge of material printability, it was until recently that some extrusion based 3D printing techniques have been applied to fabricate graphene 3D periodic architectures (Zhu et al., 2015, García-Tuñon et al., 2015). In both work, pure GO (graphene oxide) solution is modified in respect to the rheology behavior to match their extrusion based process. In Zhu's work, Fumed Silica was added in the GO suspension (40 mg ml^{-1}) to achieve highly viscous and shear thinning non-Newtonian fluids. Branched copolymer surfactant (BCS) and Glucono-δ-lactone (GδL) are added into the GO solution in Esther's paper. However, these extrusion based 3D printing approaches suffer from several disadvantages. First, these complex GO suspension manipulation process accompanies more complicated post-process thereafter, such as etching of the silica filler in hydrofluoric acid solution, which will cause some residual of the fillers in high risk. Second,

the extrusion is a continuous printing process, only simple rod-like structures are possible to print; moreover, commonly used nozzles are several hundred micron in diameter, and thus it cannot achieve the desired dimensional accuracy. Third, a common issue for layer manufacturing is bonding between two layers, this issue is especially prominent in extrusion based process such as Fused Deposition Modeling (FDM).

In this paper, a novel process for printing macro and micro controllable 3D graphene aerogel based on directional freezing technology is presented. Similar technology has been utilized to develop Rapid Freeze Prototype (RFP) 3D printing process, which is a novel Additive Manufacturing (AM) technique that can build three-dimensional ice objects directly from computer-aided design (CAD) models by depositing and rapidly freezing specific liquid droplets layer by layer. Some related research has been done based on this process (Barnett et al., 2009, Ossino et al., 2009, Bryant et al., 2003, Zhao et al., 2010, Leu et al., 2000, Liu and Leu, 2007, Sui and Leu, 2003, Bryant and Leu, 2009). However, only water was used as printing material, which can mainly be used for visualization and molding purpose with very limited applications. In this paper, we utilize this technique to rapidly freeze the water based graphene oxide (GO) droplets into ice crystal on a cold sink substrate as low as -20 ºC. The dilute pure aqueous GO suspension not only removes the addition of silica filler which otherwise will affect the aerogel structure integrate, it also allows to fabricate lower density and larger surface area aerogel due to the low GO concentration. Unlike the continuous extrusion based 3D printing process, which suffers from bad bonding due to weak intermolecular diffusion as well as the undesirable voids between the adjacent filaments. In our developed process, when the liquid solution is deposited on top or side of the previously frozen material, it partially melts the already frozen material. These two materials will be mixed together and refreeze under low temperature environment. As the re-melted aqueous material possesses low viscosity, the voids are instantly filled by the liquid material under surface tension and gravity. Since the deposited materials bind with the previous layer firmly through hydrogen bond, high structures integrity of the final assembled graphene aerogel can be achieved. Moreover, our process is based on drop-on-demand micro-dispensing technology, a nozzle with 80 micron is used to print the GO solution, which means ultra-tiny feature can be formed. Our preliminary findings show that the proposed technique can not only control the macro-scale architecture but also manipulate micro-scale morphology with high accuracy possibility (Zhang et al., 2016).

The remainder of the paper is organized as follows. In section 2, we overviewed the proposed system including the hardware configurations, software used and control system. In section 3, we proposed the process planning schematic for this presented process, and the key parameters are discussed. In section 4, we outlined the main steps to prescribe the GO solution for our printing process. In section 5, the mechanism of directional freezing is discussed. In section 6, we present the experiment results and show some finished 2.5D and 3D graphene aerogel structures. Finally we conclude and discuss future work in section 7.

2 Experimental setup

2.1 Hardware Configuration:

A Fused Deposition Modeling (FDM) based 3D printer is retrofitted to work as the host device of our project. The XY positioning precision of the printer is12 microns, and Z positioning precision is 5 microns. Figure 1 (a) shows the main components in the configuration. A peltier is

used as the cold plate, and mounted together with a heat sink to move up one layer each time during printing. A solenoid equipped syringe is mounted on a medium that can move along XY axis to travel along designed path in the printing process. The syringe is pressurized using a Nordson Performus™ V dispenser with certain pressure. The two solenoid contact pins are connected to the solenoid drive which is then connected with an Atmega2560 board. The physical setup of the whole system is shown in Figure 1 (b).

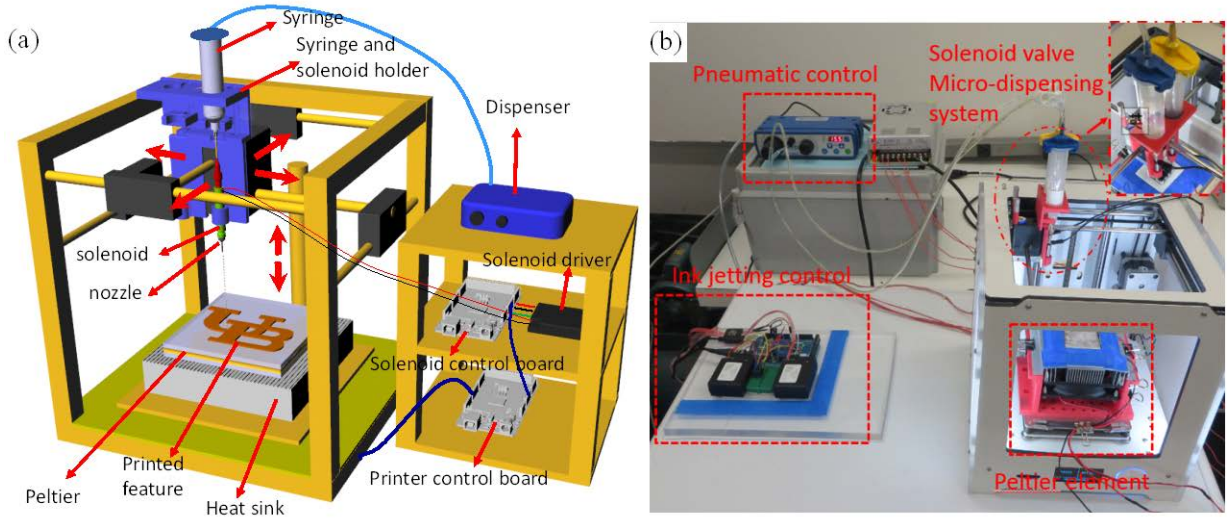

Figure 1 Designed model and the physical model

The Atmega2560 board is used to control the micro-dispensing solenoid from THE LEE CO. A code is developed and burn into the Arduino board to control the ON/OFF status of solenoid. Four parameters are required to input at the Arduino serial monitor window to instruct the board, including pin number to teach which pin is active, vibrating status to control whether the pin vibrates or not, frequency of the vibrating, and duty cycle of each vibrating.

2.2 Software and control System

The motion of printer is controlled by the generated G-code, and all the travel uses linear interpolation, no circle interpolation is needed. To coordinate the motion of printer and dispensing of solenoid value, the connection between the extra Atmega2560 Arduino board and the one in the printer needs to be built. For multi-material printing, the g-code is modified so that when it shifts between different materials, one solenoid is disabled and the other is activated. Third, for two successive layers, a waiting time is added in the code so that the layer to drop on is fully frozen.

3 Process planning

3.1 General fabricating process

The GO ink is controllably ejected onto a cold plate with a certain amount of flow rate and moves following a designed routing. GO ink is instantly frozen to ice after deposited onto the cold plate which is around temperature of -20oC. The as-formed 3D periodic graphene oxide lattice (PGOL) is then submerged into liquid nitrogen to be firstly frozen in critical cooling conditions about -190 oC after the process of 3D printing is finished, and then placed in an ultralow temperature chamber (-80 oC) for 24h to implement further ice crystallization. 3D PGOL aerogel is obtained by followed freeze drying process for 48 h. Finally, the PGOL is thermally annealed at 1000 oC for 1 h in a tube furnace under argon atmosphere to obtain periodic graphene lattice (PGL)

with highly conductive and lightweight properties. This process is shown in Figure 2. The aqueous GO suspension and water are loaded in two reservoirs (a). Computer program converts the input 3D model into machine command and control the nozzle jetting and motion, and the materials are selectively dropped onto a cryogenic substrate (b, c). The 3D printed ice structure is immersed into liquid nitrogen for further self-assembly of GO sheets (e). After the ultra-low temperature treatment, the green part is frozen under -80 oC for 24 hours (f) and the water is removed by freezing and vacuum drying for another 24 hours (g). The freezing dried part is then reduced by thermal reduction (h) and the final graphene aerogel with ultra-low density is produced (i).

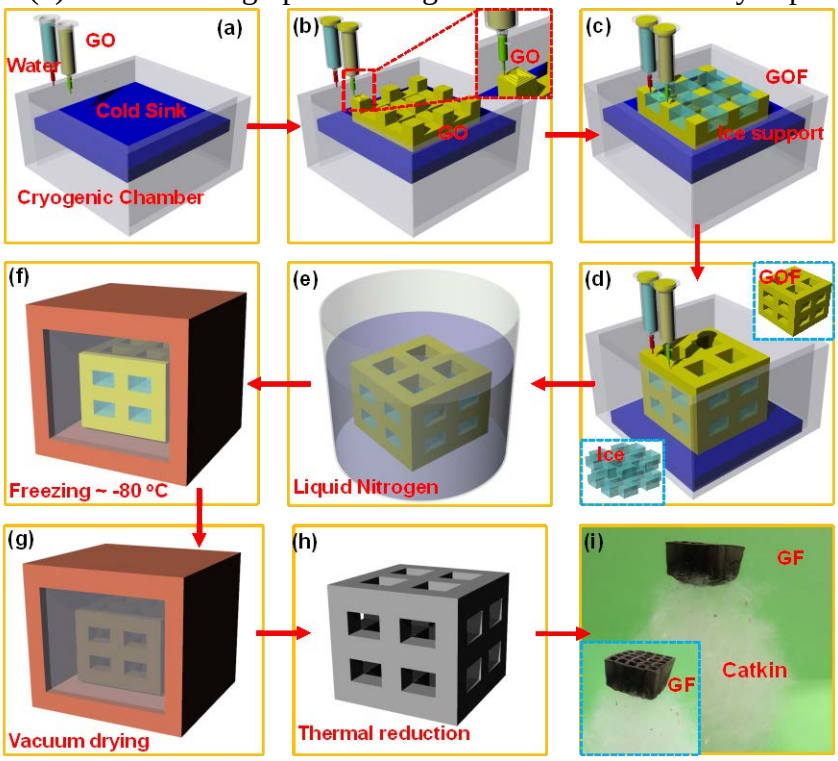

Figure 2 Graphene Aerogel fabricating process

3.2 Printing process

As a sub-section of the whole fabricating process, the graphene oxide printing process is fundamentally important. A CAD model of the print is designed; the CAD model is converted to .STL format; the STL file is then sliced using a prescribed software with delicately tuned parameters; the generated G-code is modified specifically so that it can be recognized by our retrofitted printer; finally the G-code is uploaded to the host software for printing. This printing process is shown in Figure *3*. Unlike other 3D printing process, in which support needs to be specifically designed to both minimize the material consumption and mechanically hold the part, the support material in an aqueous dispensing process is simply the negative shape of the part with regarding to its minimum bounding box. However, the ideal support material should satisfy some requirements. First, preferably similar rheology behavior is expected so that they can form unity contact angle upon dropped which is necessary to get a smooth surface. Second, the support material needs to share similar freezing temperature with the matrix material so that they can freeze similarly in one set up, more ideally they have similar latent heat. Finally, the support material needs to be easily removed in post process. The water used in our process naturally satisfies all

these requirement since the majority of our GO solution is also water, and all the water will be sublimated from solid phase to gas phase directly in the freeze drying process.

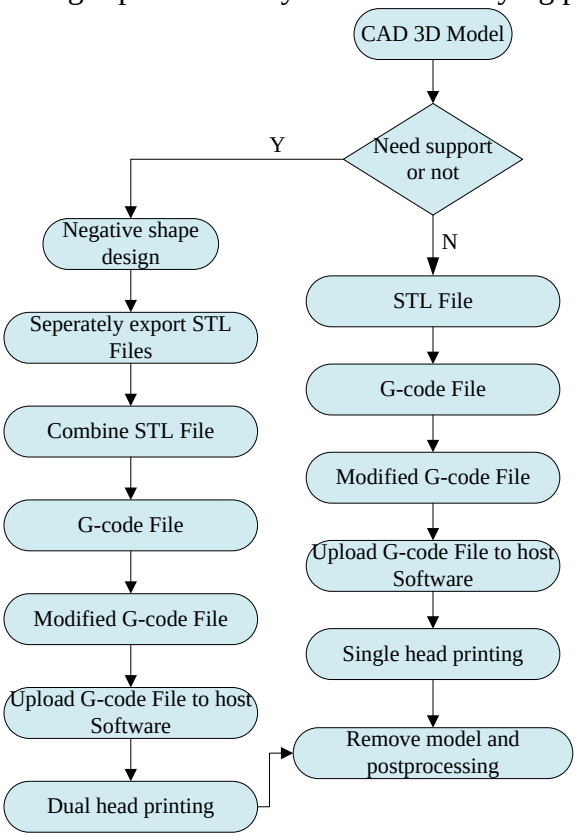

Figure 3 Graphene oxide printing process

3.3 Path planning

For a liquid deposition, a 100% infill should be the proper density otherwise liquid will flow anywhere that is not filled in previous layer. Figure 4 (b) shows a typical rectilinear infill pattern. Figure 4 (c) shows the path planning of a layer of model in (a) with graphene oxide only, and Figure 4 (d) shows the path planning of a multi-material layer of the model, the red-framed portion is water, and the rest is printed with graphene oxide.

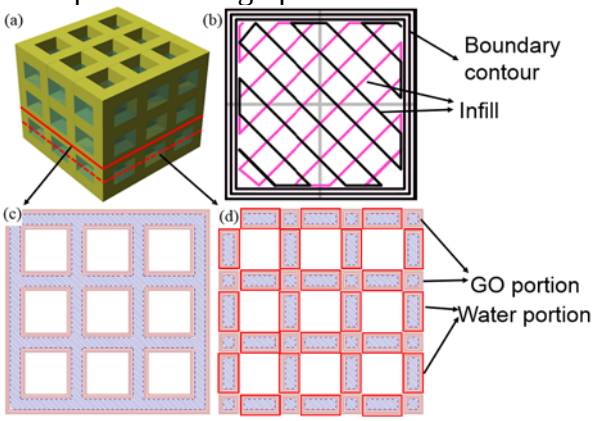

Figure 4 Path planning (a) A model of lattice with support (b) Rectilinear infill pattern (c) A layer with only graphene oxide (d) A layer with both graphene oxide and water

4 Material preparation

GO ink Preparation: Single layer GO precursor was purchased from Cheap Tubes Inc. (USA) with average size of 300-800nm lateral dimensions and 0.7-1.2 nm layer thickness, which was synthesized by a modified Hummers' method featured 40-60% functional group content (C: 35-42%, O: 45-55%, H: 3-5%) providing high solubility in DI Water with high purity of 99 wt.%. GO powder was ultrasonically dispersed in DI water to prepare uniform suspension with concentration of 10 mg/ml. An agent ethylenediamine (EDA) was mixture with GO suspension by volume ratio of 2‰ to prepare the 3D printing used GO ink. The mixture of GO and EDA was ultrasonically dispersed for 0.5 h to make it uniform and then added NaOH solution (Concentration= 5%) by volume ratio of 5‰ for adjusting the viscosity of ink to be suitable for ink-ejecting process. The stacking GO sheets are bonded by π-π attraction which is classified as non-covalent bonding. The weak non-covalent bonding between the GO sheets cannot fully unlock the exotic properties of the 2D graphene sheet. Our primarily results show that the chemical covalent bonding between the GO sheet surface and the reduction agent can give rise to improved mechanical, thermal and electric properties. And EDA serves as the reducing and functionalizing reagent in our process, it play an important role in the assembly of graphene oxide sheet. Figure 5 illustrates how the EDA (in the middle) bonds up and down two different GO layers.

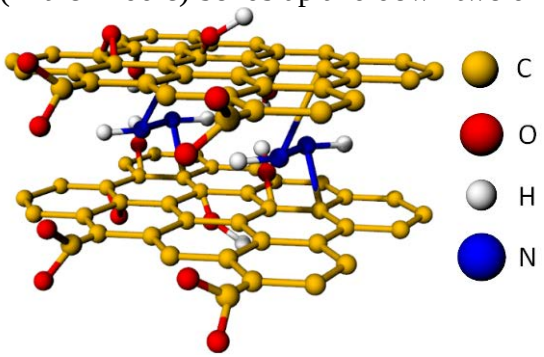

Figure 5 Schematic illustration of mechanism of EDA bonding with GO layers

5 Freeze casting

Freeze casting (also known as ice templating) is a technique that takes advantage of the anisotropic solidification behavior of a solvent (Generally water) with well dispersed solute (Extensively ceramic slurry) to form a directionally porous structure. The first observation of cellular structures resulting from the freezing of water can date back to more than a century ago (Lottermoser, 1908). However, it wasn't until 2001, when Fukasawa created directionally porous alumina castings (Fukasawa et al., 2001), that the idea for using freeze-casting as a means of creating novel porous structures really set sail. Since then, research has grown considerably in this area. Freeze casting has been used to fabricate metal/ceramic and model polymer/ceramic (poly(methyl methacrylate); PMMA)/alumina and, more recently, PMMA/SiC hybrid materials with fine lamellar or brick-and-mortar architectures (Deville et al., 2006, Liu et al., 2014, Munch et al., 2008, Roy et al., 2010, Wegst et al., 2014).

In the situation of graphene oxide, a well-dispersed partially reduced GO dispersion is frozen, pr-GO sheets are concentrated at the boundary of ice crystals and then aligned along the growth direction of ice due to the squeezing effect. As a result, a continuous honeycomb-like network is formed (Qiu et al., 2012, Hunger et al., 2013). The mechanism of the freeze casting to form ice crystals repelling the GO particles is illustrated in Figure 6 (a). After the well dispersed GO sheets is frozen, they are expelled by the ice crystals and aligned along the crystal growth

direction. Due to π-π attraction between the GO sheets and the functionality of EDA, the assembled network was found to be very stable and maintain its structure integrity upon sublimation of ice which finally results in the formation of highly organized hierarchical porous structure (*Figure 6* (c)-(d)).

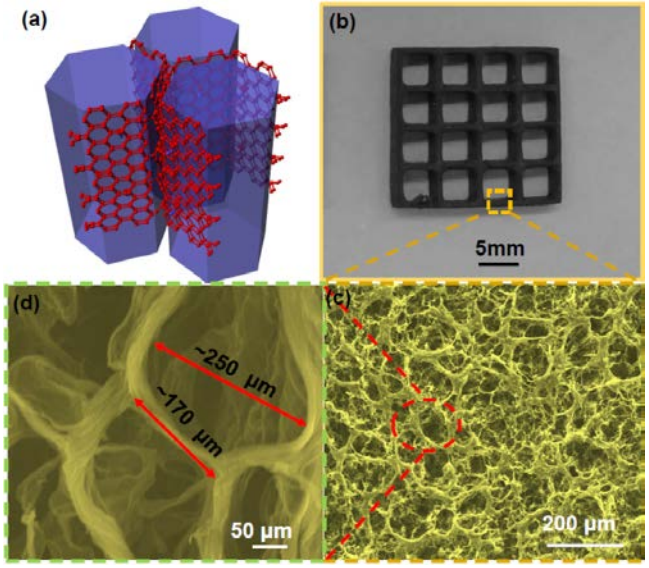

Figure 6 the formed micro structure of 3D printed Graphene macro structure (a) Growing ice crystals expel 2D graphene oxide particles into crevice (b) Macro image (c)-(d) The large magnification SEM image of surface morphologies with hierarchical porous nanostructures (pore size ~ 250 μm, facial-link length ~ 170 μm)

6 Results and discussions

This paper developed a novel 3D graphene aerogel fabrication process. The process is composed of two major parts. One part is 3D printing graphene oxide, we have experimented with our machine for a bunch of different structures including 2.5D network, grids, 3D lattice, turbine, gears etc. The other part is forming final graphene aerogel, for each printed sample, we carefully processed them to form final aerogel.

6.1 Printed graphene ice structures

Several structures have been successfully built including 2.5D sensor networks (Figure 7 (a)-(b)), in which each cross section in Z direction is same. This type of structure is stable and relatively not that challenge to print. Comparing to 2.5D structure, truly 3D structure is more difficult to print, however, we still successfully printed some samples, Figure 7 (c) shows a turbine impeller printed. Upon close inspection, each blade is clearly formed. Figure 7 (d) is a 3D lattice structure, this part needs support as shown in the process. The challenges currently in our project lies in the frosting problem, which is mainly because of the temperature gradient around the print area. Upon investing to get a cold chamber, we expect this problem can readily be resolved.

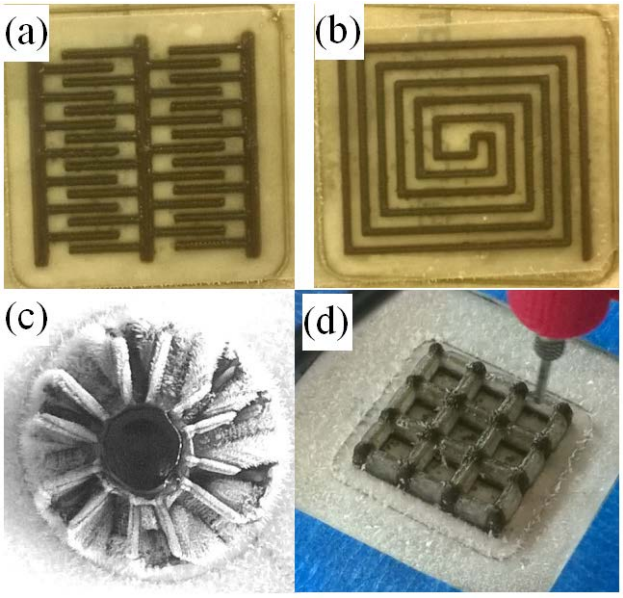

Figure 7 3D printed graphene oxide ice structures (a)-(b) Strain sensor network (c)-(d) Turbine rotor and truss 3D structure

6.2 Aerogel formation

Graphene aerogel is the terminal product to fabricate in this project. After the printing is finished, the prints are transferred to a -80 ^{o}C freezer through liquid nitrogen box. The samples are then put in a freeze drying machine for super critical drying. Figure 8 (a)-(b) shows some of the freeze dried GO samples. We found that constant chamber temperature is a key factor for successful samples. To verify the success of formed aerogel, some performance tests are implemented, in Figure 8 (c), the aerogel is put on top of catkin, we can see the aerogel well stand without any depress on the catkin. In Figure 8 (d), the printed aerogel is connected between LED and power supply, the LED is lighted up. More properties test can be found in our previous work (Zhang et al., 2016).

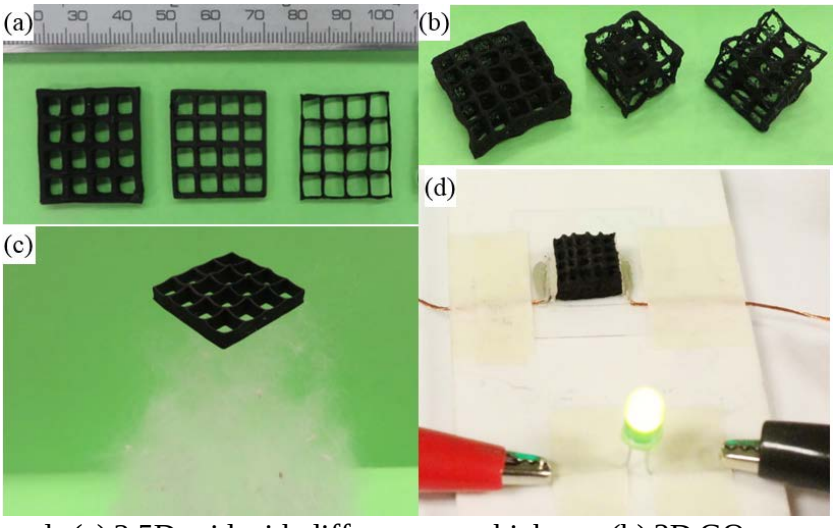

Figure 8 GO aerogels (a) 2.5D grid with different strut thickness (b) 3D GO aerogel periodic lattice of different size (c) Lightness test (d) Electrical conductivity test

7 Conclusion

A novel directional freezing based 3D printing of graphene aerogel process has been presented. The proposed system utilizes micro-dispensing technology to dispense GO water solution in a drop-on-demand manner onto a cold plate with specific temperature gradient, the dropped GOs freezes instantly upon landing the plate. By fully taking advantage of both 3D printing technology and freeze casting mechanism, macro and micro controllable truly 3D graphene aerogel can be fabricated. A process plan which covers the complete process and printing process for the developed system is proposed. An illustration of the directional freezing mechanism specifically for graphene oxide material is provided. A collection of successful samples are printed including 2.5D grid structure, special network, 3D graphene lattice, spatially varying 3D structure, and multiple material prints. Some future work includes: (1) Optimize parameters for the printing process to achieve high-quality, high-accuracy prints; (2) Study GO solution Rheology behavior to get the optima flow rate; (3) Study heat transfer between frozen layer and newly deposited layer to realize both bonding and surface quality; (4) Develop a path planning algorithm specifically for aqueous solution, more specifically for our graphene oxide solution.

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