

# Novel 3D Graphene-Based Materials Prepared by Chemical Vapor Deposition: Process Development and Production Scaling-Up

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## ABSTRACT

We have developed methods of CVD processing which are suitable for the industrial production of graphene foam. By optimizing the parameters of CVD growth and choosing the proper nickel support structure, we have tuned the graphene foams overall porosity, aspect ratio, and density. This allows for better mechanical stability and electrical conductivity, improving the graphene foams performance. To optimize graphene foam's energy storage capabilities, we have chemically modified the surface of the graphene foam. With these advancements, graphene foam is on the fast track to be used in commercial applications. This report will be on the advancements we have made in scaling up the production of graphene foams.

**Keywords:** Graphene, foam, three-dimensional, chemical vapor deposition, CVD, ultralight materials, graphene composites.

## INTRODUCTION

Graphene is a single atomic layer thick two-dimensional carbon material comprised of  $sp^2$ -hybridized carbons. [1] Graphene's extraordinary electrical, mechanical, and structural properties have attracted the ever-growing interest of the scientific and engineering communities. Chemical Vapor Deposition (CVD) has been proven as the technique of choice to manufacture meter-scaled high quality single [2] and few-layered graphene [3] films that are now commercially available. Recently, the CVD method has been taken to the third dimension with the advent of freestanding, ultra-lightweight graphene-based materials.

The ability to architecture three-dimensional graphene structures could result in materials that possess high a surface area, are mechanically robust, and electronically conductive. In addition, these materials can be further chemically functionalized, as well as mixed with polymers and other materials.

An attractive method that competes with the methods described here which also have the potential for large-scale industrial production is to use self-assembly of the chemically derived form of graphene, graphene oxide (GO) [4]. Chemical oxidation of graphite involves the oxidation of graphite, exfoliation of GO, and, if desired, reduction of the obtained GO. Various three-dimensional structures were prepared from GO using this method, but the electrical conductivity of such films suffers from intrinsic defects embedded in graphene oxide lattice. As a result, practical use of these structures is limited.

Novel approaches employ the use of metal catalytic supports to create three-dimensional graphene materials. Chen *et.al.* pioneered the use of commercial nickel and copper foam substrates as a catalytic template for CVD graphene growth. [5] Similarly, inexpensive nickel powders with the specific size of 30 microns can be used as a growth support [6]. Furthermore, this method can be expanded by the mixing of particles of various shapes and forms to tailor the material properties.

Herein, we focus on three-dimensional graphene foams made via CVD processing using nickel foams as a template. Porous nickel foams are commercially produced and are made via low-temperature CVD, in which nickel carbonyl is decomposed in the presence of a catalyst and a carrier gas. The nickel is deposited on a polyurethane (PU) foam substrate. The resultant foams are effectively replicates of the PU foam structure. [7] Nickel foams find use in many applications such as in fuel cells, cellular materials, and batteries.

Graphene foams may also be used in energy storage devices, such as supercapacitors and batteries. The graphene foam has a high surface area because of its porous nature, giving it a high electrochemical capacitance and opens the potential to store massive amounts of energy. [9] Graphene which is directly precipitated on nickel foam has good electrical contact with the nickel foam, further improving its performance as a supercapacitor. Graphene foam on nickel was found to have a specific capacitance of

816 F g<sup>-1</sup> at 5 mV s<sup>-1</sup>, which is high when compared to other metal oxides. [8]

In addition, it has been demonstrated that inexpensive and simple devices based on graphene foams can be utilized for chemical sensing with a high sensitivity and reversibility. Such graphene sensors were found to be about ten-times more sensitive than ones currently on the market, detecting 20 ppm of nitrogen dioxide. The graphene sensors were able to detect gases at room temperature, while many commercial sensors today require high temperatures to work properly. The porous graphene is not only more effective than current commercial sensors; it also can easily be reused. In order to free the graphene foam of trapped gas molecules, all the graphene needs is an electric shock. [10]

## METHODS AND RESULTS

The 3D graphene foams were prepared via CVD by the procedure proposed by Zongping Chen et al. [5]. A sample of open-cell nickel foam was placed inside a quartz tube reactor and heated to 1000°C in the atmosphere of argon. Then, the reaction gas mixture consisting of argon, hydrogen, and methane was introduced and flown for 30 minutes – then the reactor was rapidly cooled. The SEM image of the multilayer graphene foam is shown in Figures 1, and 2.

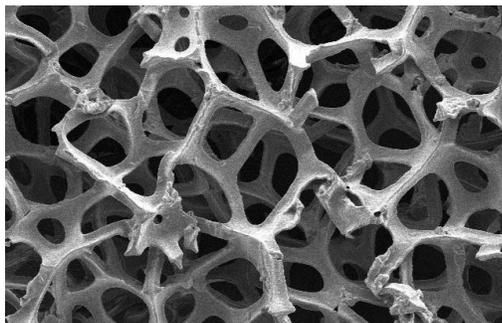


Figure 1: SEM Image of 3D Graphene Foam, low resolution



Figure 2: SEM Image of 3D Graphene Foam, medium resolution

Ripples of the graphene film formed during the cooling down can easily be seen in Figure 3.

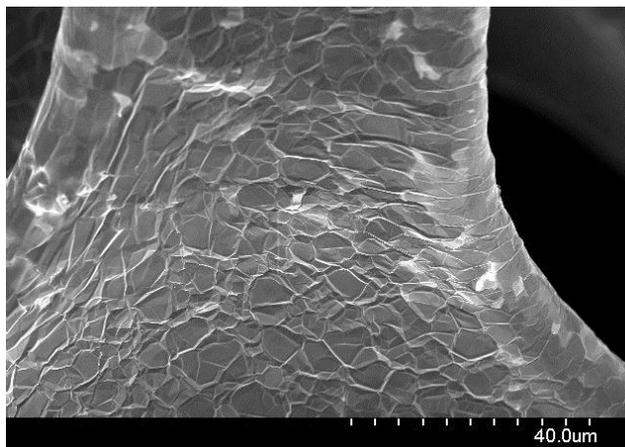


Figure 3: SEM Image of 3D Graphene Foam, high resolution

To prepare the free standing graphene foam, we placed the sample into 1M solution of FeCl<sub>3</sub> in water warmed up to 65 C. Once the nickel had been completely removed, the sample was then carefully transferred into a vessel with DI water and finally to the vessel with methanol. Then the sample was taken out of methanol and dried.

Figure 4 shows the comparison of Raman spectra before and after nickel removal. No change in line shapes as well as an absence of the D-band (not in the range of the spectrum in Fig. 4) demonstrates that the foam remains intact during the treatment.

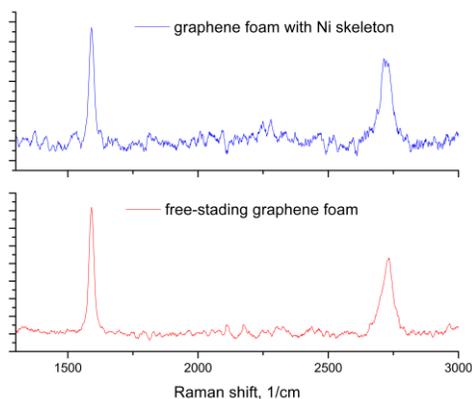


Figure 4: Raman spectra of three-dimensional graphene foam before and after nickel removal.

To prepare samples of the foam decorated with nanoparticles, we put a droplet of aqueous suspension of Au and CdTe nanoparticles, and let the samples dry. Figure 5 shows the SEM image and Figure 6 shows EDX spectrum of the graphene foam decorated with CdTe nanoparticles.

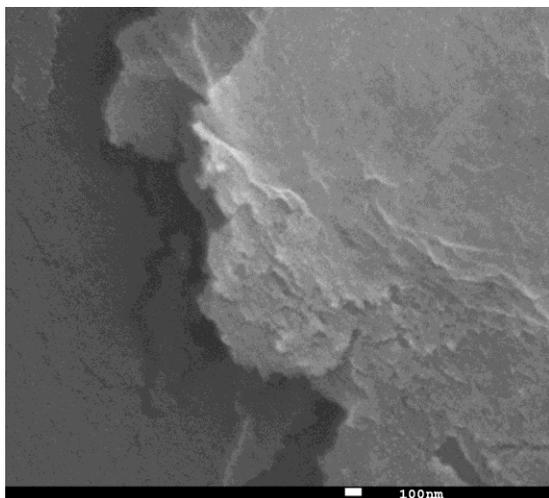


Figure 5: SEM Image of 3D Graphene Foam decorated with CdTe nanoparticles.

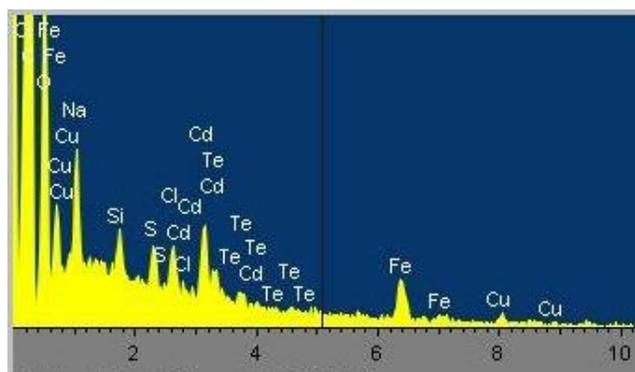


Figure 6: EDX Spectrum of 3D Graphene Foam decorated with CdTe nanoparticles. The presence of the Fe and Cu atoms is due to contamination of the foam during the etching of the Ni scaffold.

Figure 7 shows the Raman spectra of the pristine free-standing graphene 3D foam, as well as the graphene foam decorated with Au and CdTe nanoparticles. The spectrum of the pristine foam is drastically different from the spectrum of the foam decorated with nanoparticles.

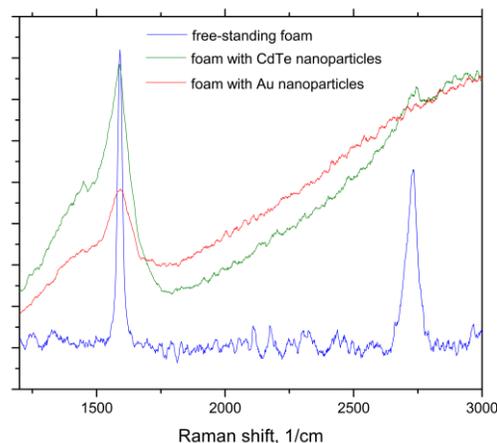


Figure 7: Raman spectra of the pristine free-standing graphene 3D foam as well as the graphene foam decorated with Au and CdTe nanoparticles.

It is well known that Raman spectra of nanoparticles in the region in the Figure 7 are dominated by vibrational modes of the capping agents. Notably, the peaks between  $1330$  and  $1500\text{ cm}^{-1}$  and between  $1570$  and  $1580\text{ cm}^{-1}$  are attributed to the symmetric and asymmetric stretching modes of the carboxylates, respectively. [11]

## SUMMARY

We demonstrated a simple and effective route for the production of three dimensional graphene-based structures as well graphene/metal composite materials. Raman spectroscopy has been proven to be a sensitive tool for graphene-nanoparticle interaction. We envision that the described technique can be easily adapted for the production of advanced graphene-based sensors, fuel cells, and energy storage devices.

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