

Three-Dimensional Printed Graphene Foams – Supporting Information

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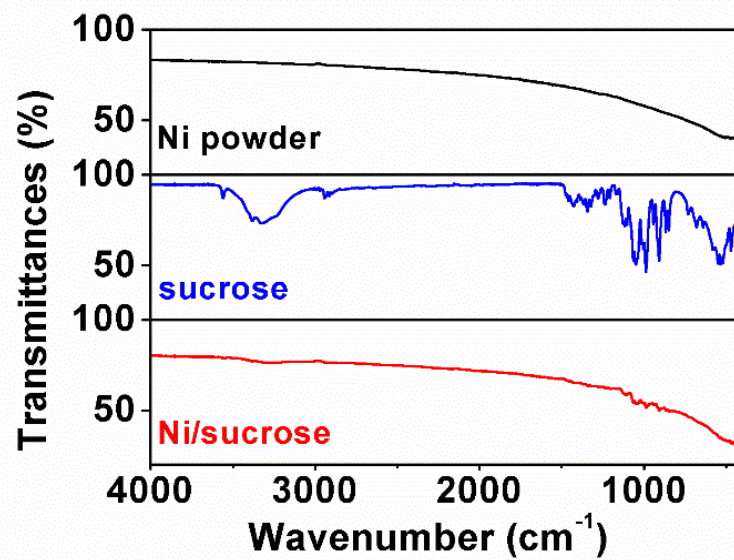


Figure S1. ATR-IR spectra of Ni powder, sucrose, and Ni/sucrose hybrid powder.

As shown in Figure S1, sucrose absorbs light $\sim 1000\text{ cm}^{-1}$ ($\sim 10\text{ }\mu\text{m}$). Ni absorbs at low wavenumbers. Thus, a $10.6\text{ }\mu\text{m}$ CO_2 laser, which should heat both Ni and sucrose, was employed in this work to grow graphene.¹⁻² Based on known graphene growth mechanisms, the Ni particles will be sintered and sucrose will decompose to generate atomic C. The C will dissolve in the hot Ni and precipitate during the fast cooling process to form multi-layered graphene on the Ni surface.

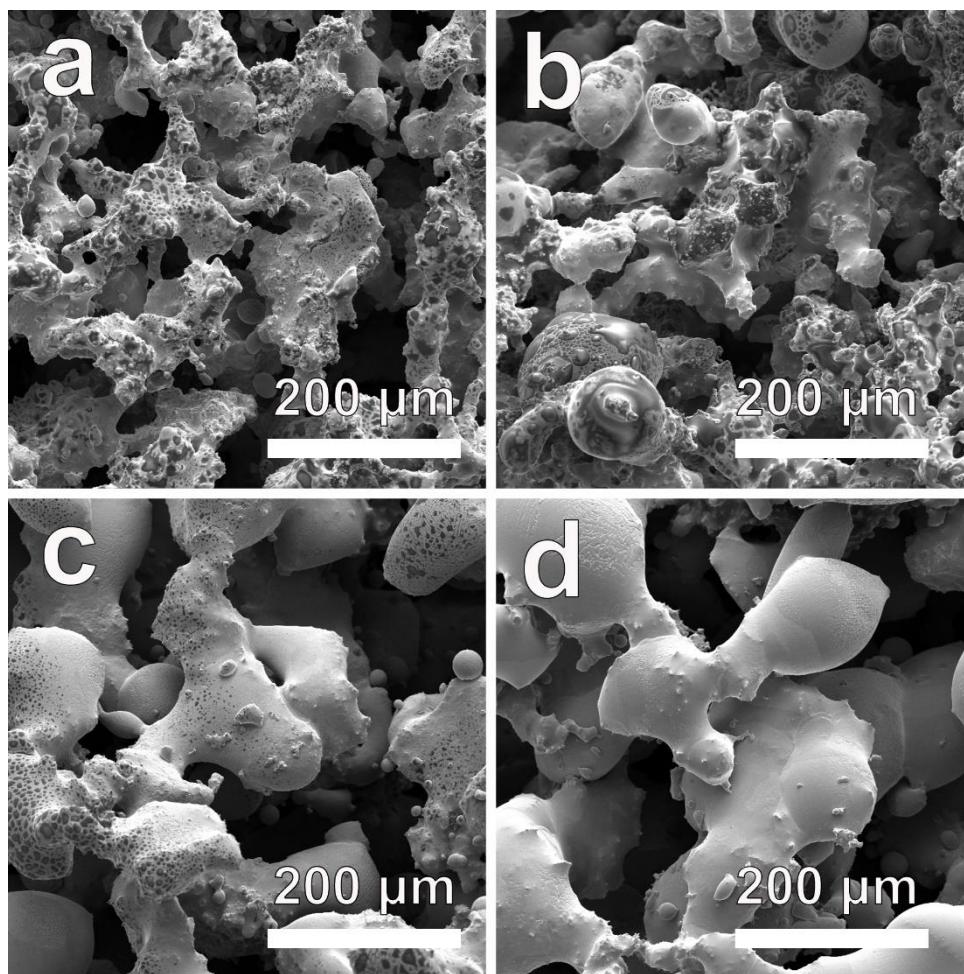


Figure S2. Low magnification SEM images of 3D printed GFs with Ni scaffold prepared using 100P and (a) 5S, (b) 3S, (c) 2S, and (d) 1S in a H_2 atmosphere.

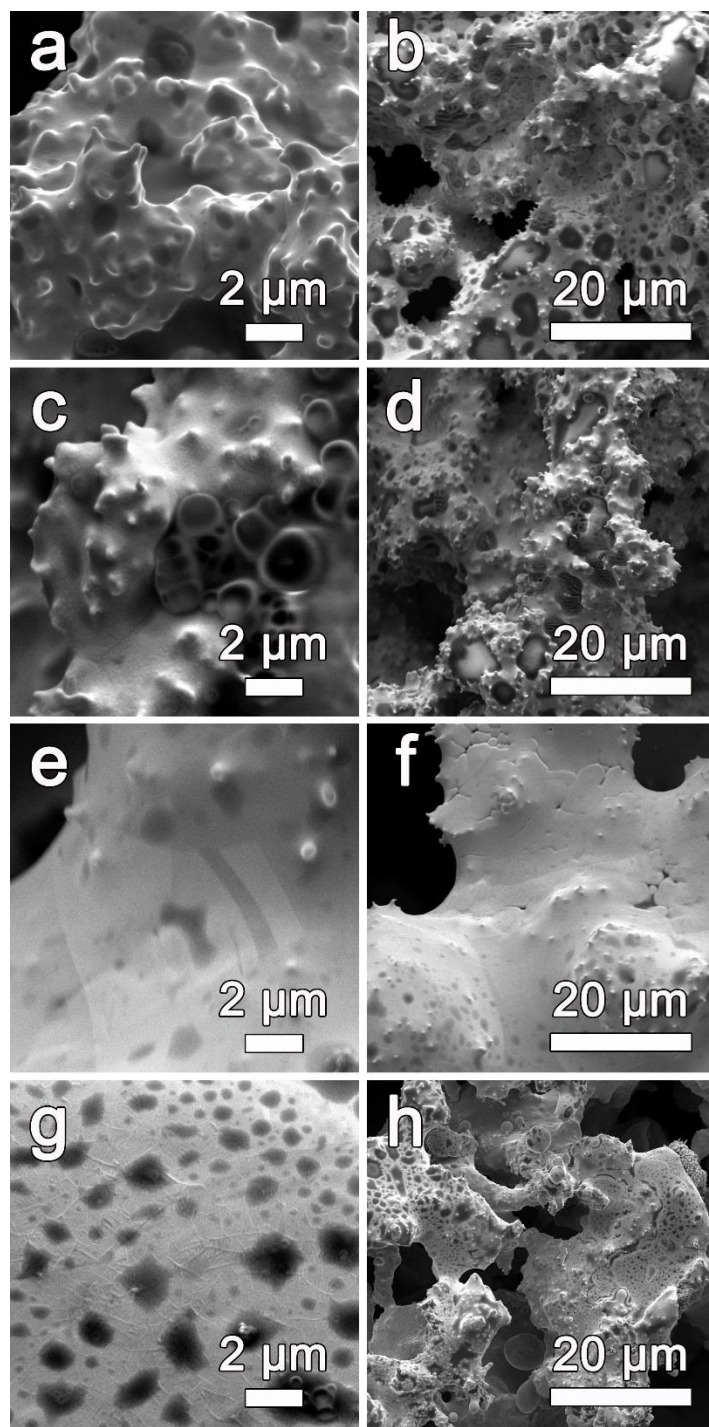


Figure S3. SEM images of 3D printed GFs with Ni scaffold prepared using 5S and (a-b) 10P, (c-d) 20P, (e-f) 50P, and (g-h) 100P in a H_2 atmosphere.

The effect of changing laser duty cycles was systematically investigated at a constant rastering speed of 5S. With lower laser duty cycles of 10P and 20P, graphene was not detected on the surface of the Ni scaffolds, as shown in Figure S3a-d. When increasing the laser duty cycle, graphene with wrinkled features was observed on the surface of the Ni scaffolds. Even at a duty cycle of 100P, large amounts of unreacted sucrose was still observed, indicating that the 5S rastering speed of was too fast. The laser duty cycle of 100P was chosen in the next experiments.

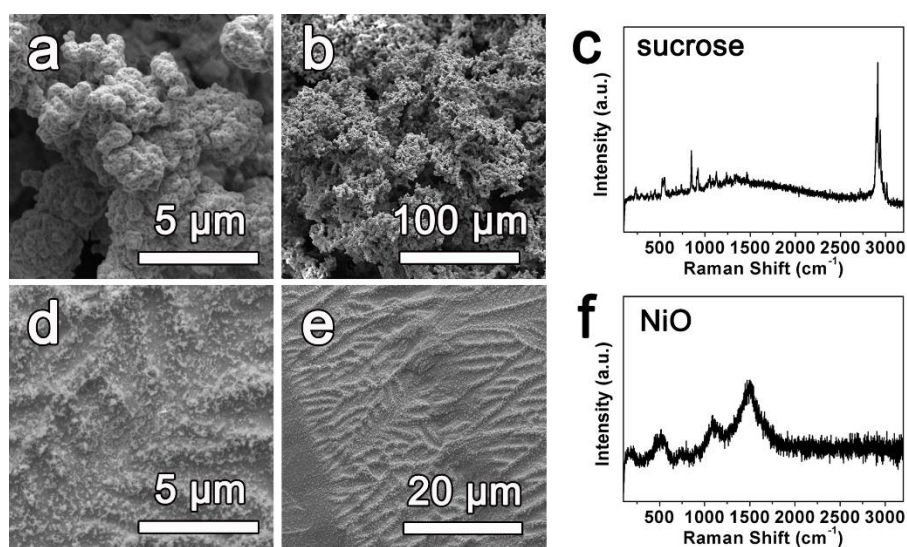


Figure S4. (a-b) SEM images and (c) Raman spectrum of Ni/sucrose mixture without laser treatment, and (d-e) SEM images and (f) Raman spectrum of the sample prepared using 100P and 2S in air.

The untreated sucrose coated Ni particles were analyzed by SEM, as shown in Figure S4a-b. The Ni particles were aggregated, with sucrose apparently acting as a binder. The charging effect was observed during SEM operation, indicating the low conductivity of the Ni/sucrose mixture. The sucrose on the surface was detected by Raman spectroscopy, as shown in Figure S4c.

The 3D printing process was performed in air using a laser duty cycle of 100P and rastering speed of 2S. As shown in Figure S4d-e, a large number of particles are observed on the surface of the sintered Ni scaffolds, and little or no graphene was present. The Raman spectrum in Figure S4f displays NiO_x signals, and no graphene-based D, G, or 2D bands. It is presumed that the sucrose was burned away by the laser in air; the Raman analysis shows the Ni was oxidized. Based on this result, the laser reaction should be done in an inert or reducing (H_2) atmosphere.

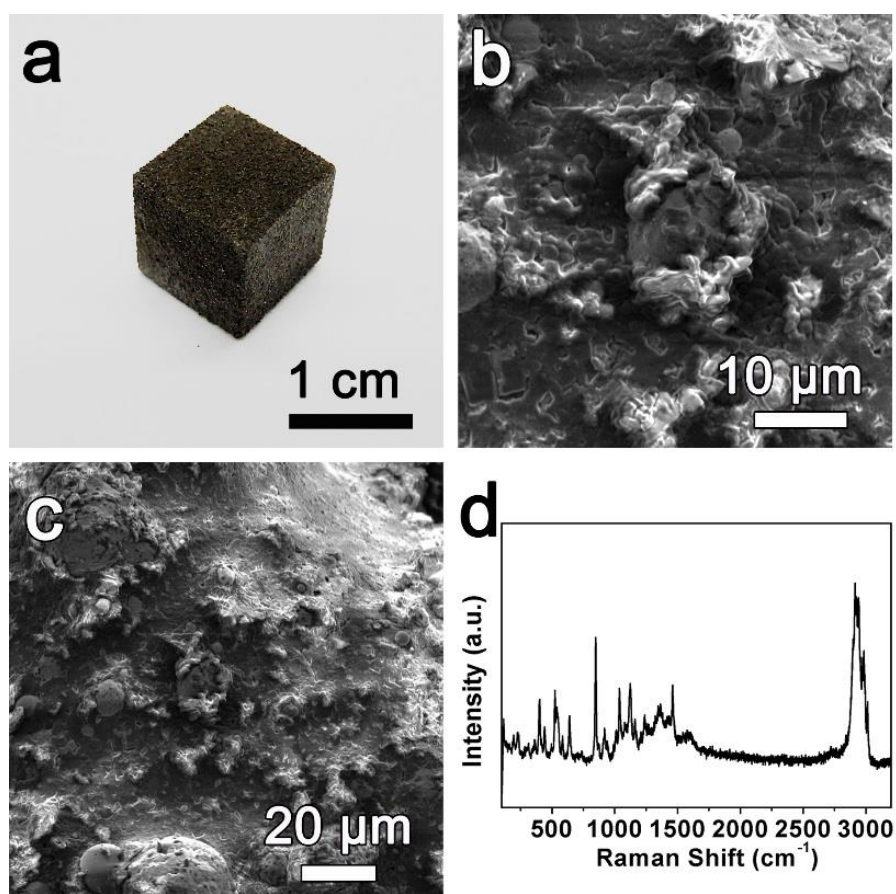


Figure S5. (a) Photograph, (b-c) SEM images, and (d) Raman spectrum of a 3D printed sample prepared using the same mixture of Ni and sucrose but with a commercial fiber laser 3D metal printer at 20 W of power and 100 cm/s rastering speed in a N_2 -flushed atmosphere.

We tried synthesizing 3D GFs using a commercial automated 3D metal printer (Concept Laser, Mlab) at Qualified Rapid Products Company. The 3D metal printer was equipped with a 1.06 μm fiber laser system. The samples were printed under a N_2 -flushed atmosphere. As shown in Figure S5a, a 1 cm $\times$ 1 cm $\times$ 1 cm product was obtained. However, the SEM images (Figure S5b,c) indicate the lack of graphitic structures and the presence of what is assumed to be unconverted sucrose. Ni particles, rather than sintered Ni scaffolds, were observed. We presume the sucrose melted under the high heat conditions and acted as a binder in the cubic sample, instead of decomposing. The Raman spectrum in Figure S5d shows no graphene. This result indicates that the use of a 10.6 μm CO_2 laser is necessary to make 3D GFs, while the 1.06 μm fiber laser is not absorbed by the Ni and sucrose mixture in accordance with the absorption data in Figure S1.

References.

1. Lin, J.; Peng, Z.; Liu, Y.; Ruiz-Zepeda, F.; Ye, R. Q.; Samuel, E. L. G.; Yacaman, M. J.; Yakobson, B. I.; Tour, J. M. Laser-induced Porous Graphene Films from Commercial Polymers. *Nat. Commun.* **2014**, 5, 5714.
2. Peng, Z.; Ye, R.; Mann, J. A.; Zakhidov, D.; Li, Y.; Smalley, P. R.; Lin, J.; Tour, J. M. Flexible Boron-doped Laser-induced Graphene Microsupercapacitors. *ACS Nano* **2015**, 9, 5868-5875.