**Supporting information**

1. Material synthesis

The Ni template was printed using a FORWARD LM180 SLM System, Harbin Forward Multidimensional Intelligent Device Co. Ltd. The processing parameters are as follows: the laser power of 200 W, scanning speed of 1000 m/s, hatch spacing of 0.07 mm and layer thickness of 0.04 mm. The unit cell of the 3D-printed Ni scaffold is of square shape with strut length around 1 mm and wall thickness around 390 μm. A small piece of 5.4 mm (L) x 5.4 mm (D) x 7.0 mm (H) was used for study. To improve the surface finish, the as-received template was annealed at 1370°C for 9 h under Ar and H_2. The annealed template was then put in a tube furnace for subsequent graphene growth via a standard CVD. Briefly, the 3D template was first activated at 1000°C for 10 min under Ar flow of 180 ml/min and H_2 flow of 200 ml/min, then followed by the injection of the styrene carbon source at a rate of 0.254 ml/h controlled by a syringe pump (Razel Scientific Instrument, INC. USA), still under the same mixture gas flow for 1 h. Finally, the sample was cooled down naturally to room temperature under a reduced Ar flow of 50 ml/min. The 3D graphene networks were obtained by refluxing the Ni/graphene composite in 3 M HCl at 80°C for at least 3 days to remove the Ni template, and the final product was checked by energy-dispersive X-ray spectroscopy (EDS). Scheme S1 illustrates the key steps for the synthesis of the 3D graphene.
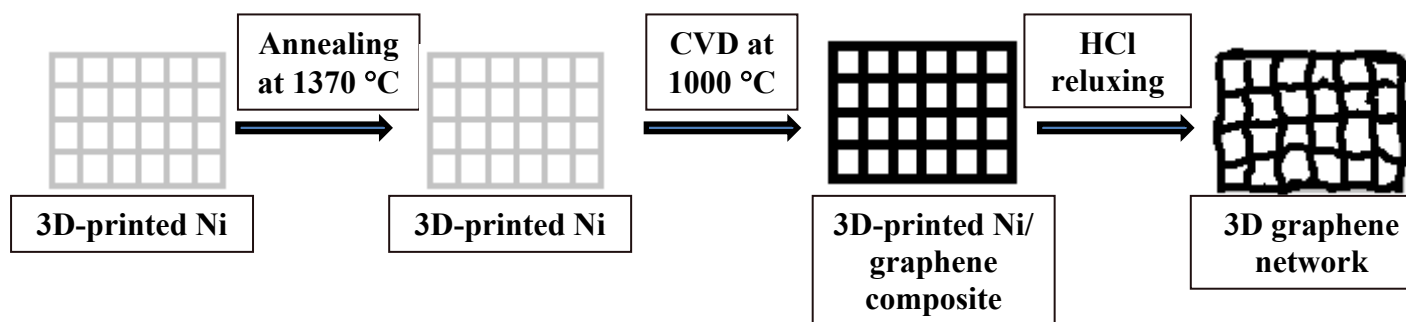
Scheme S1: Schematic illustration of the 3D graphene network creation.

2 Material Characterisation

3D imaging of the annealed Ni template was performed using an *X-tek BenchTop 160Xi CT* scanning system, in which the sample was X-rayed over 360 degrees to create a 3D model of the sample. Scanning electron microscopy (SEM) images and EDS were recorded using a JSM6390LV microscope operated at 20 kV. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 operated at 200 kV. For the TEM sample, a piece of

the as prepared 3D graphene/Ni networks was probe sonicated in acetone, then the suspension was dropped onto a holey carbon coated copper grid (300 mesh, Agar). Raman spectra were acquired using a Renishaw RM1000 Raman microscope (RENISHAW, Wooton-Under-Edge, UK), with excitation at 532 nm and a 50 × microscope objective lens.
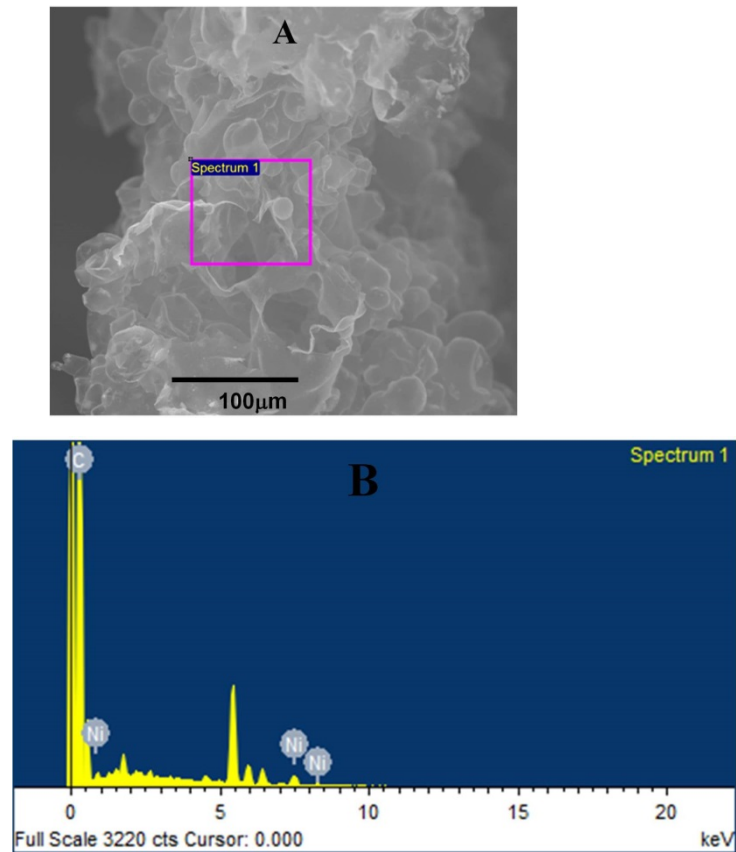

Fig. S1 SEM image (A) and corresponding EDS results (B) obtained from the selected box in the image of 3D graphene networks after the removal of the Ni (C content is 97.5wt% and Ni is 2.5wt%)
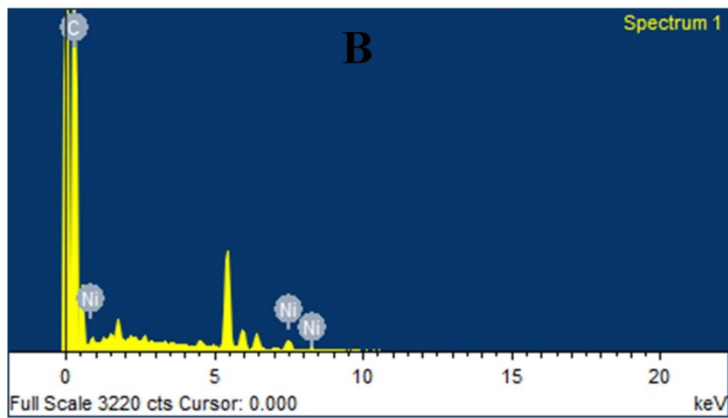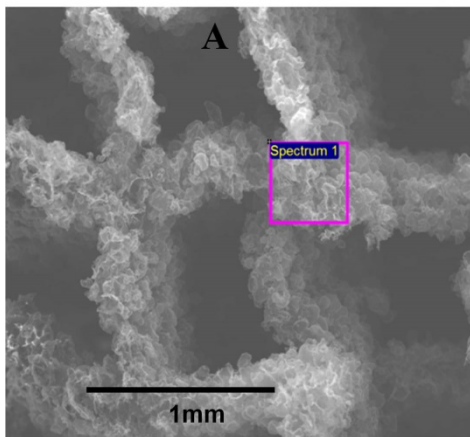
Fig. S2 SEM image (A) and corresponding EDS results (B) obtained from the selected box in the image of 3D graphene networks after the removal of the Ni (C content is 98.6wt% and Ni is 1.4wt%)