Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Synthesis and processing of graphene hydrogels

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Experimental section

Materials

Graphene (xGnP graphene nanoplatelets, Grade M) used in this study was commercial obtained from XG Sciences, Inc. (USA). Grade M graphene platelets typically consist of aggregated of sub-micron platelets that have a particle diameter of about 5 microns and a typical particle thickness of about 10 nanometers. Sodium deoxycholate (SDC) was purchased from Kishida Chemical Co., LTD (Japan).

Methods

Graphene-based hydrogel was synthesized by mixing graphene and SDC in a defined ratio in water and then applying ultrasonic treatment for several hours with the assistance of ball-milling, as described elsewhere[1]. The ultrasonic-treated samples were black sol and were aged for 24 hour until they changed to gel. A series of samples was prepared with mass concentrations of graphene ($Ø_{graphene}$) of 1%, 2%, 3%, 4%, 8%, and 12%, and mass concentrations of SDC ($Ø_{SDC}$) of 10%, 20%, 30% and 40%. SEM and TEM studies were performed using a Hitachi SU-70 field-emission SEM (Hitachi, Japan) and a JEM-2100 TEM (JEOL, Japan). Optical photographs were taken by a polarizing microscope (Eclipse LV100POL, Nikon, Japan). X-ray diffraction were measured by an Ultima IV X-ray diffractometer (Rigaku, Japan). Raman spectra were measured by a LabRAM ARAMIS Raman spectrometer (Horiba, Japan) operated at room temperature and using 532 nm (2.33 eV) laser excitation. The rheological properties were evaluated with a HAAKE Rheostress 600 system (Thermo Scientific, German) operated at 20ºC. The nanopartterns were directly written by SHOT mini 200α (Musashi Engineering, Inc., Japan) using graphene-based hydrogels as a “solid ink”. I-V response measurements were performed using a current pulse generator (HC-11, Hokuto Denko, Japan) to supply a stable current and an R6452A digital multimeter (Advantest, Japan) to record the voltage. The graphene-based hydrogels were completely dried in air before the electrical conductivity measurements.

[1] Z. Tan, S. Ohara, M. Naito, H. Abe, *Adv. Mater.* 2011, **23**, 4053.

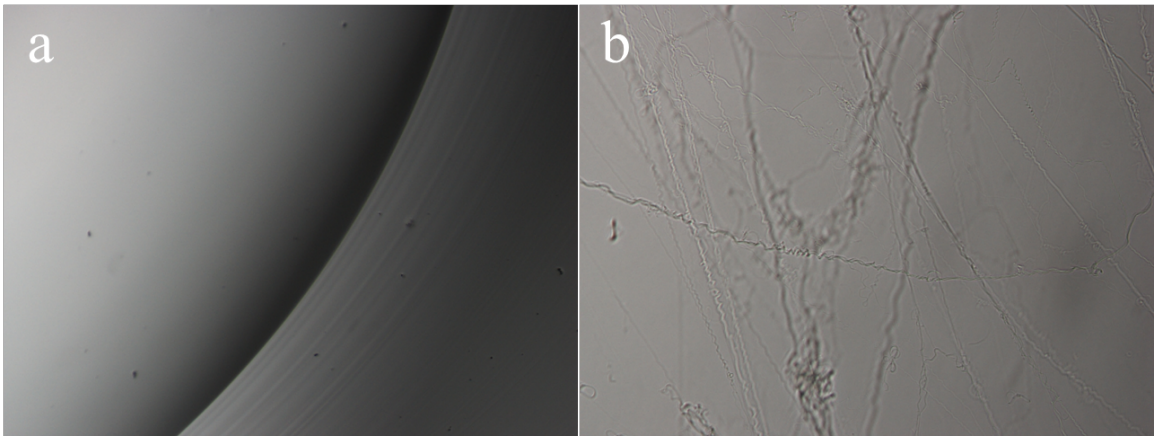

Figure S1 | Optical microscopy images of a pure SDC aqueous suspension. a, SDC aqueous suspension with $Ø_{SDC}$ = 10%. No fibrous self-assembly was observed at this concentration of SDC. **b,** SDC aqueous suspension with $Ø_{SDC}$ = 20%. Fibrous self-assembly of SDC was observed in this case.

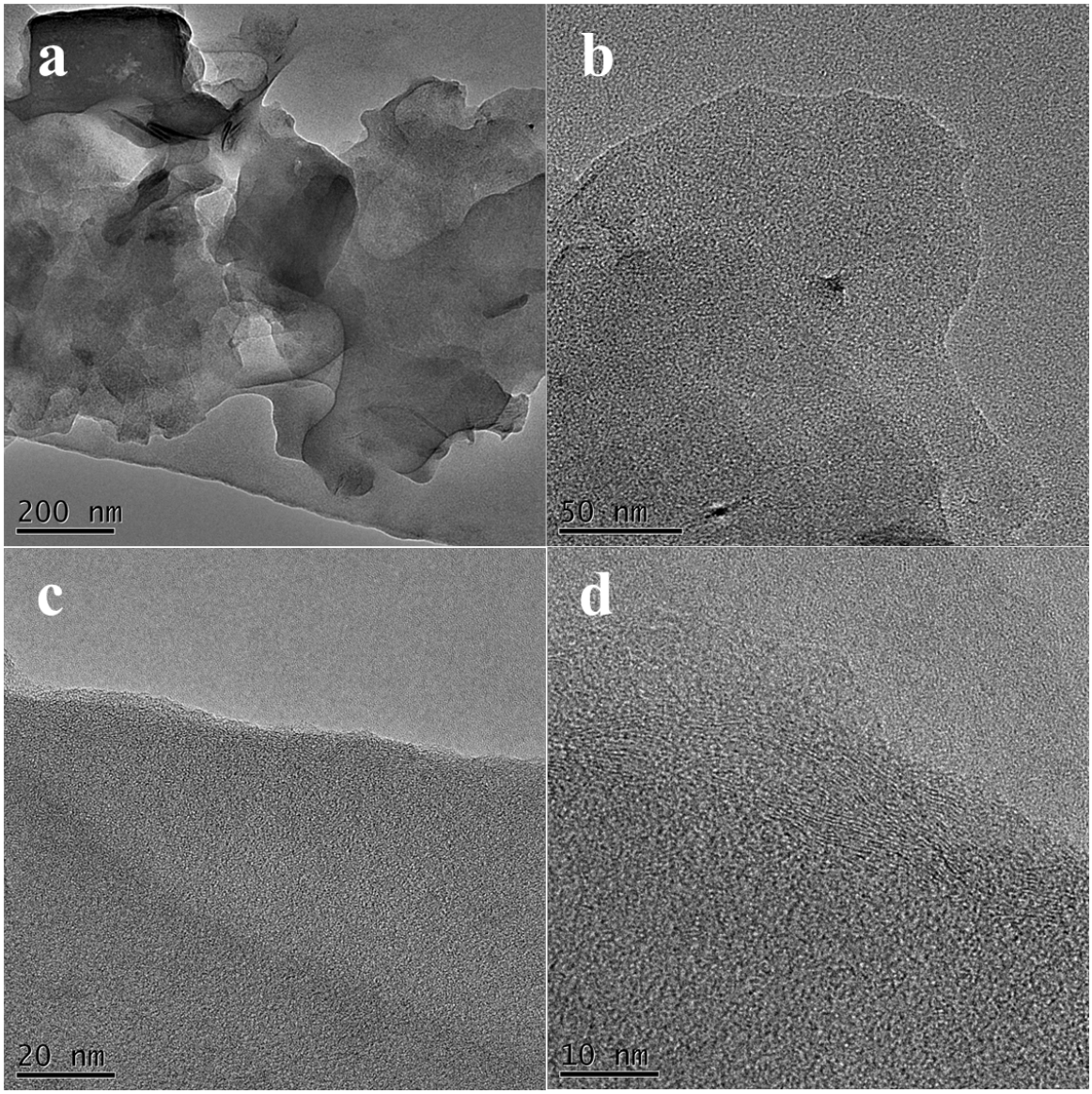

Figure S2 | TEM images of pure graphene.

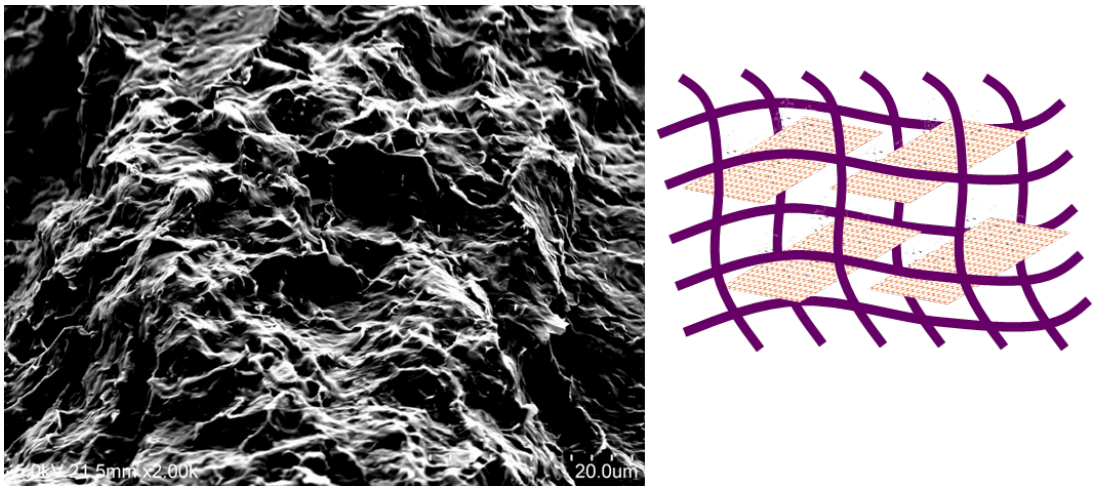

Figure S3 | Surface morphology of graphene-SDC hydrogels at a 45º angle view. The surface of the graphene hydrogels is covered by the self-assembly of SDC nanotubes.

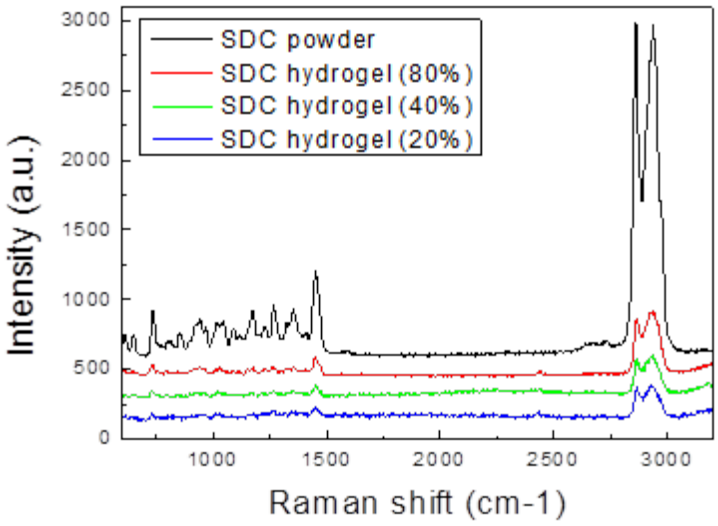

Figure S4 | Raman spectroscopy of pure SDC powder and SDC hydrogels with various contents of 20, 40, and 80%. SDC powder exhibits two strong, sharp characteristic Raman peaks at 2862 and 2940 cm^{-1} accompanied by many fingerprint peaks at a range from 500 to 1500 cm^{-1}. The Raman peak at 2940 cm^{-1} and 2862 cm^{-1} were assigned to CH stretching vibrations.

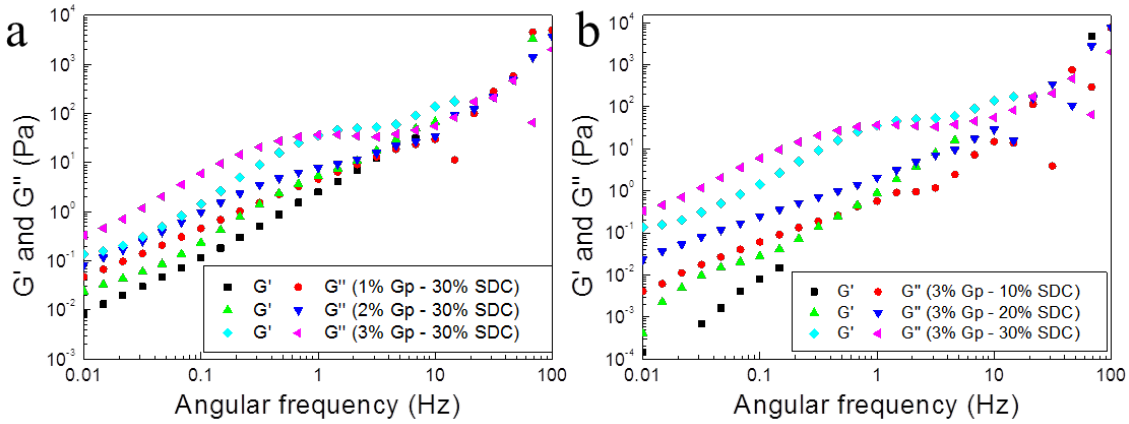

Figure S5 | Rheological properties of graphene-SDC hydrogel at low loading content. a, b, Elastic modulus (G') and viscous modulus (G'') of hydrogels as a function of angular frequency.

Figure S6 | Computer-controlled omnidirectional printing equipment for direct writing of graphene patterns. SHOT mini 200α (Musashi Engineering, Inc., Japan) was the printing part under controlled by ML-808FX which could be directly written a program for printing. An air pump was used to supply continuous pulse of compressed air. The maximum pressure of the exported compressed air was 900 KPa. The writing of graphene pattern could be controlled by adjusting the viscoelasticity of graphene hydrogels and the exported compressed air.

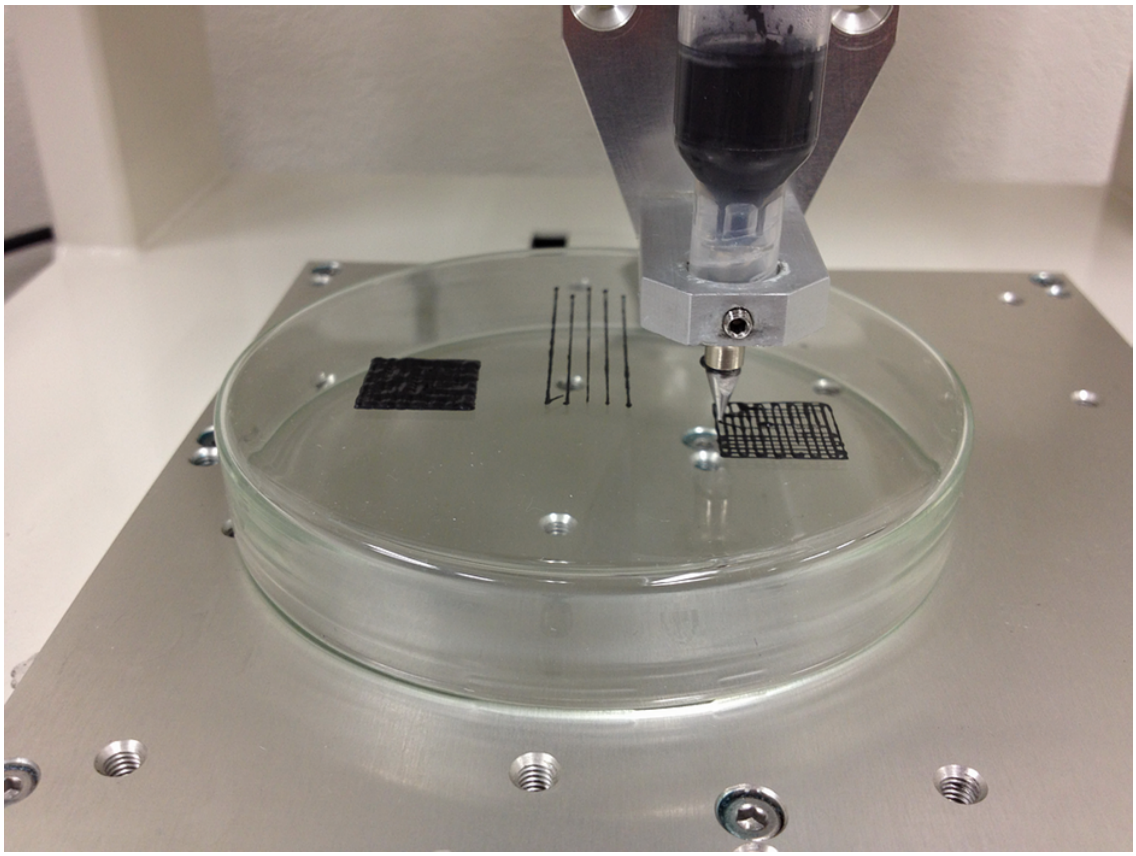

Figure S7 | Complex patterns of graphene directly written by omnidirectional printing. A multi-layered pattern was under printed by the computer-control omnidirectional printer, SHOT mini 200α.