Supplementary Information

Tube-rolling and formation of mechanically robust micro-tube in graphene oxide aqueous dispersions during shear flow

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I. Experimental Section

A. Graphene oxides

Graphene oxide was prepared using a modified Hummers method[1,2] (GO) and modified Brodie method[3] (B-GO). The average lateral size of GO and B-GO is 20.2 μm and 8.0 μm, respectively.[1,3] 0.1 wt.% B-GO and 0.1 wt.% GO dispersions with various pH was prepared. In order to adjust pH, KOH or HCl was added to the dispersions. Both B-GO and GO dispersions 0.1 wt.% was far higher than a critical LC concentration.[1]

B. Characterization methods

The rheological measurements were conducted using a controlled-stress rheometer (AR-G2, TA Instruments). A cone and plate geometry with a diameter of 40 mm was used, with a gap of 52 μm. A solvent trap was used to prevent water evaporation of GO aqueous dispersions during all rheological measurements. The bottom plate was replaced by a transparent glass plate in order to examine the morphology of the GO dispersions after cessation of flow. A spacer was located between the glass bottom plate and cone after cessation of flow. Then, the cone and plate was detached from the rheometer and the images of the dispersions were taken by a camera below the bottom plate. X-ray diffraction (XRD) of GO and rGO were analysed using an Ultima diffractometer (Rigaku, Japan) with CuK_{α} radiation at a scanning rate of 1°/min within the 2θ range of 5–80°. The slow and fast drying of the GO was conducted in a vacuum oven at 50 °C for 12 h, and at 160 °C for 3 h, respectively. The morphology of the GO and rGO was observed using a field-emission scanning electron microscope (FE-SEM, JSM6700F, JEOL, Japan). The optical and cross-polarized images of the GO were obtained using an inverted optical microscope (AE-31, Motic, China). The optical microscopic images were also obtained using microscope (ECLIPSE LV 100D, Nikon, Japan).

The 3D confocal microscopic images of GO dispersions and micro-tubes were observed with 488 nm green laser using a confocal laser scanning microscopy (LSM700, Zeiss). The PDMS microchannels were fabricated using a photolithography process.[4] The width (*W*) and height (*H*) of the microchannel are 500 μm and 130 μm, respectively. The flow rates (*Q*) in the microchannels were controlled using a syringe pump (NE-1600, New Era, USA), and the apparent shear rates are given by $\dot{\gamma} = 4Q/\pi r_H^3$ [$r_H = WH/(W+H)$]. The apparent shear viscosity of GO dispersions was calculated by measuring the differential pressure (ΔP) between two straight channels with different lengths ($\tau = \Delta P r_H/2L, \tau = \eta\dot{\gamma}$).[4] The differential pressure was measured by differential pressure transducer (PX409, OMEGA).

Table S1. Conditions for the formation of micro-tubes in the cone & plate rheometer.

	pH 2.2	pH 3.2	pH 4.0	pH 10.7
GO (0.1 wt.%)	○	x	x	x
GO (0.05 wt.%)	○	x	x	x
B-GO (0.1 wt.%)	x	x	x	x
B-GO (0.05 wt.%)	x	x	x	x

O: micro-tubes observed, X: micro-tubes were not formed.

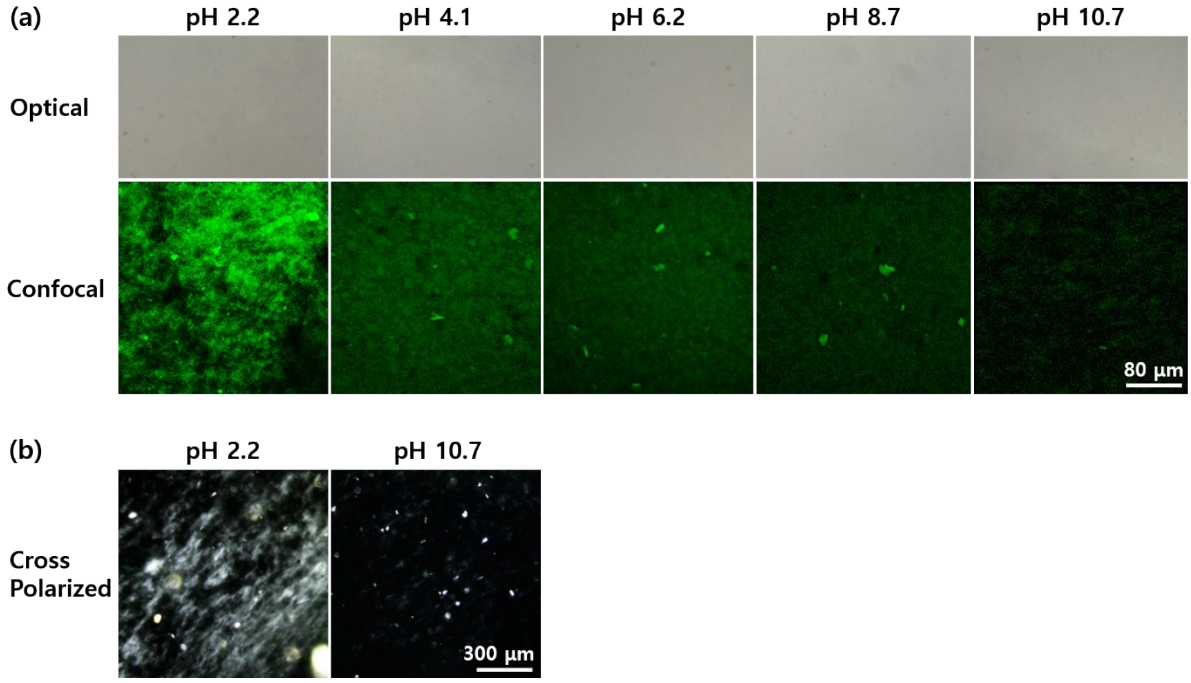

Fig. S1. Dispersion states of 0.1 wt.% GO dispersions depending on pH observed by a) confocal-, optical-, and b) cross-polarized microscopy. GO dispersions were synthesized using modified Hummers method (average lateral size of 20.2 μm).

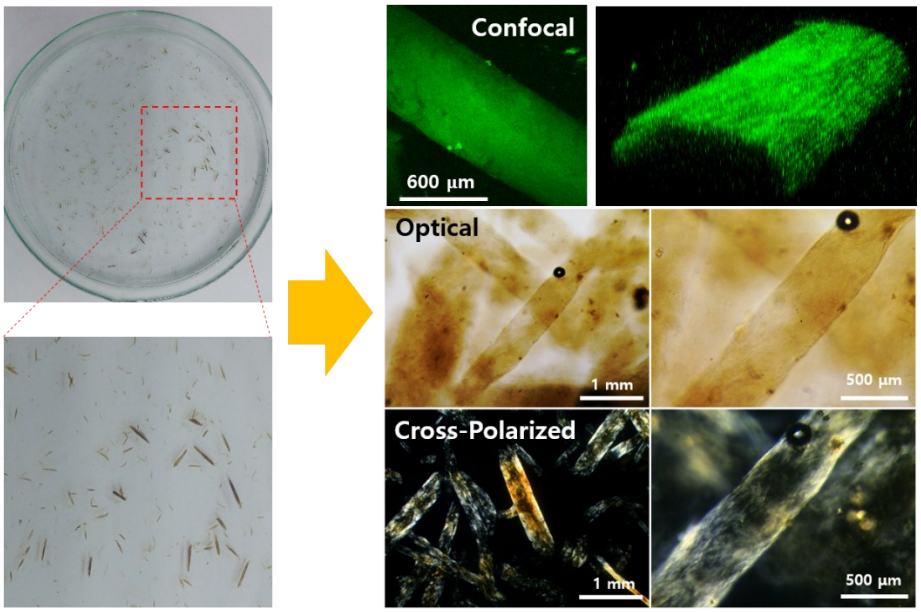

Fig. S2. Optical, cross-polarized, and confocal microscopic images of GO micro-tubes dispersed in water.

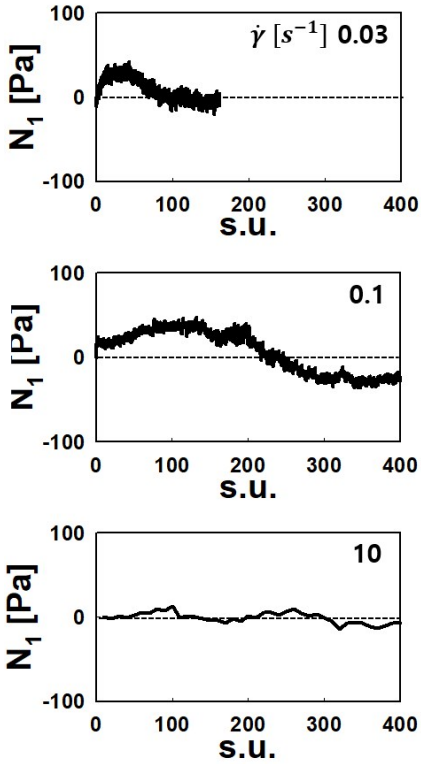

Fig. S3. The first normal stress differences of 0.1 wt.% GO dispersion at pH 2.2 at various

shear rates.

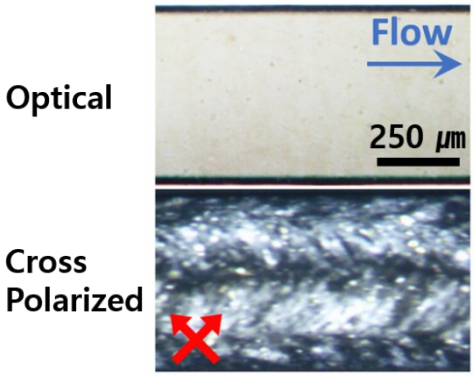

Fig. S4. Capture of the movie recorded in the micro-channel flow of 0.1 wt% GO at pH 2.2. (optical and cross-polarized images, $\dot{\gamma}$=0.6 s^{-1}); large GO domains showed during flow.

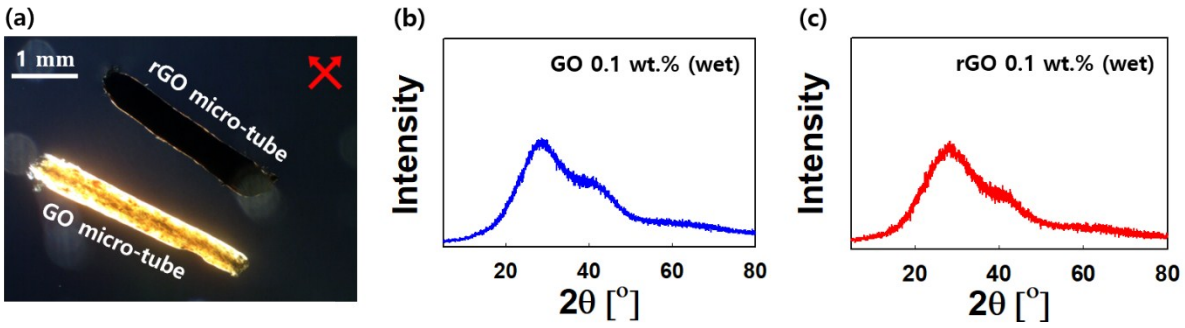

Fig. S5. (a) The cross polarized optical microscopy for as-synthesized GO micro-tube and for chemically reduced GO micro-tube by HI. XRD patterns show typical amorphous shape both for (b) as-synthesized GO micro-tube and for (c) chemically reduced GO micro-tube by HI.

References

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