Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Patterned, Morphing Composites via Maskless Photo-click Lithography

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FTIR-ATR spectra were collected with repeated scan times of 64 and a resolution of 4 cm^{-1}. The appearance of peak at 944 cm^{-1} in the chitosan-MA curve results from the out of plane deformation of –C=CH_2 in the methacrylamide structure. After functionalization, the increased absorbance of the peak at 1548 cm^{-1} and range of 560-650 cm^{-1} come from the amide II band (N-H bending and C-N stretching vibrations) and the bending motion of O=C–N, respectively [1].

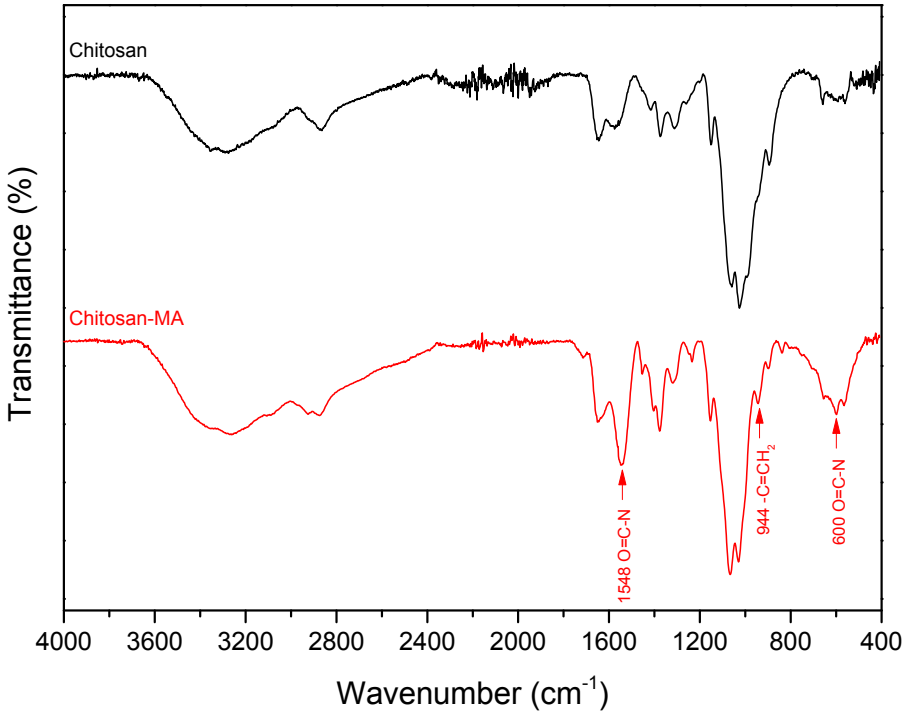

Figure S1: FTIR spectra for chitosan and chitosan-MA.

^{1}H NMR spectroscopy was conducted on a Bruker 500 MHz at 25 °C. Chitosan and chitosan-MA (0.5% (w/v)) were dissolved in 0.5% deuterium chloride (DCl) in deuterium oxide (D_2O) at room temperature. The appearance of the proton peaks at 5.28, 5.6 ppm and 1.7-1.9 ppm results from

the $–C=CH_2$ and $–C–CH_3$ groups on the methylene binding of the chitosan-MA. The methacrylation degree is determined by the integrated area ratio between the $–C=CH_2$ of the methylene group at 5.28-5.6 ppm and the H3-H6 peaks of chitosan at 3.3-4.0 ppm [2,3].

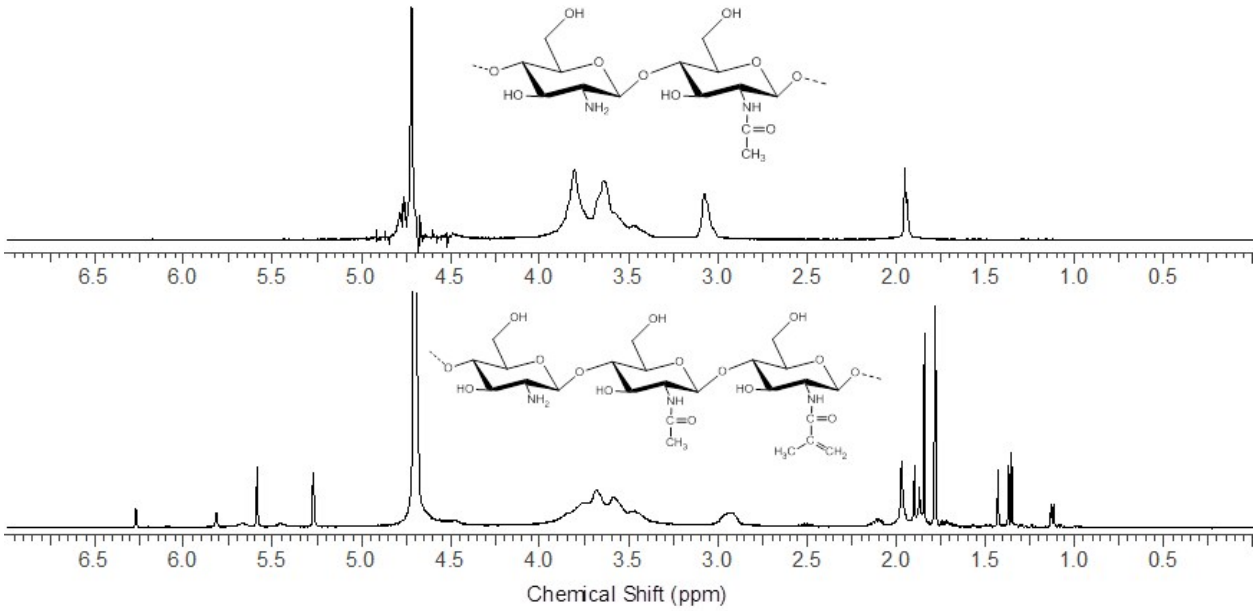

Figure S2: ^1H NMR spectra for chitosan and chitosan-MA

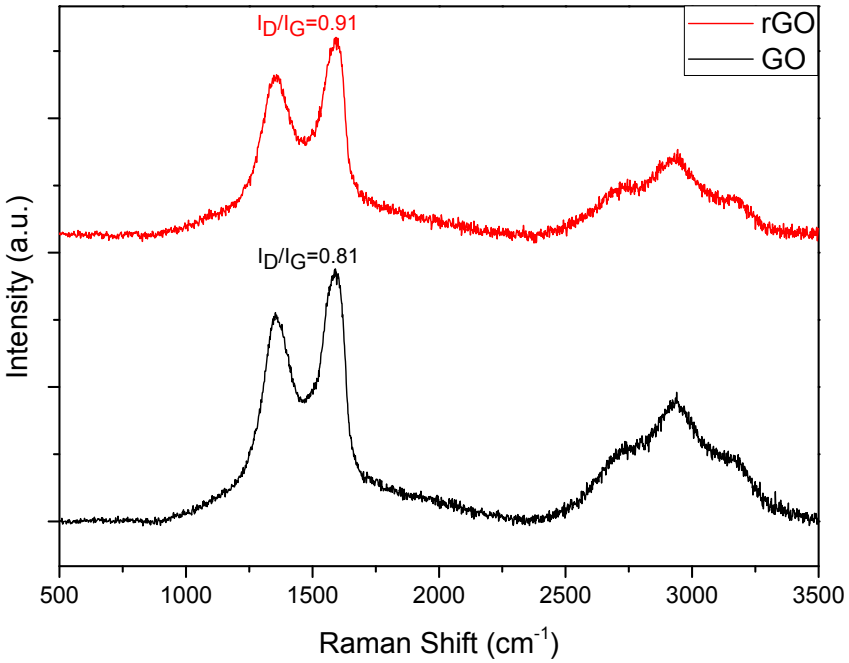

Figure S3: Raman Spectroscopy of GO and rGO

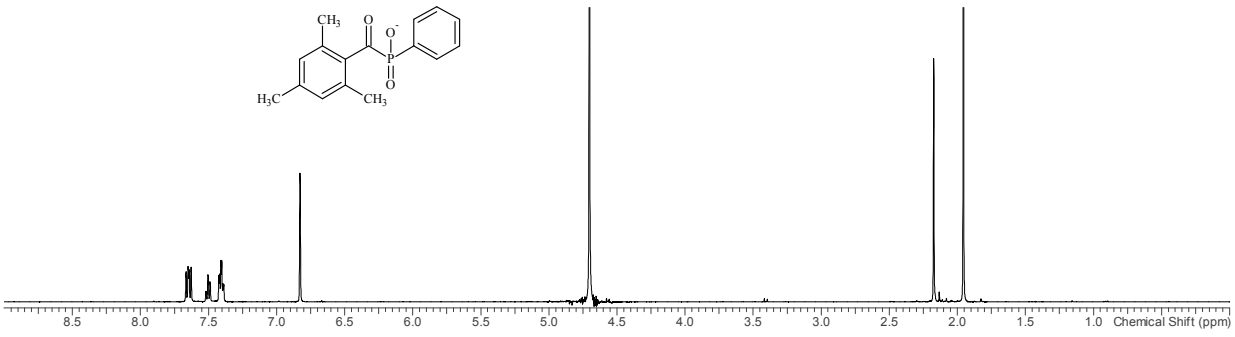

Figure S4: ^{1}H NMR spectrum for the photoinitiator, LAP

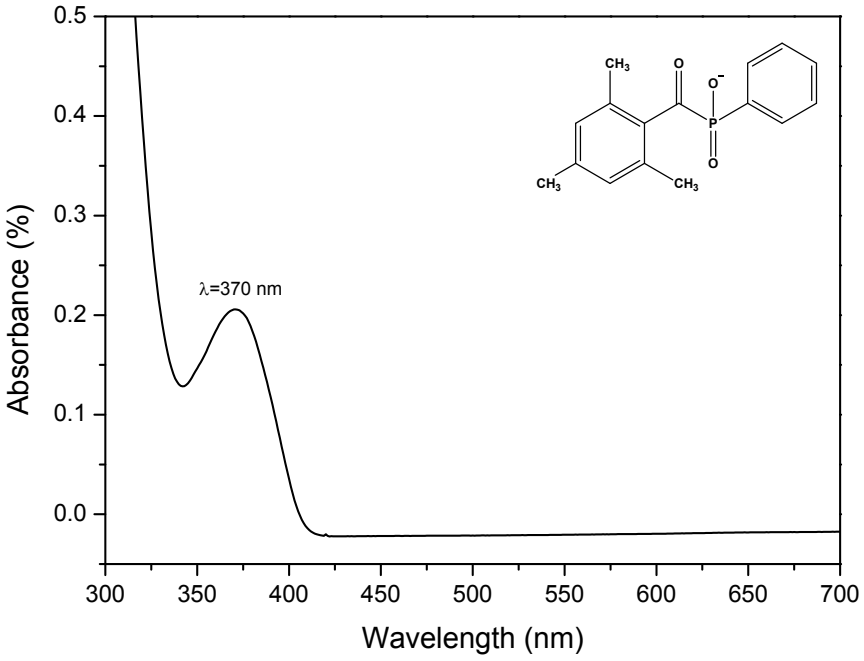

Figure S5: UV-visible spectrum for the photoinitiator, LAP

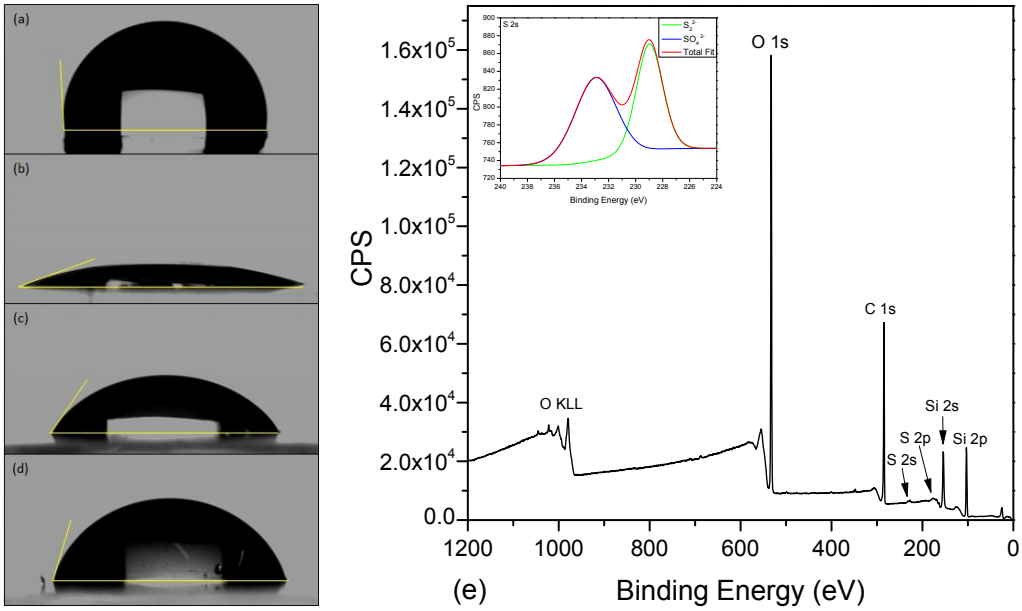

Figure S6: (a) Water-in-air (w/a) contact angle of PDMS surface before plasma. (b-d) w/a contact angle of PDMS surface after plasma treatment in 0 min, 20 min and 120 min, respectively. (e) XPS spectrum of thiolated PDMS (Inset: Deconvoluted XPS of S 2s for thiolated PDMS), the percentage of S 2s is 1.57 atom% on the thiolated PDMS surface. (Due to the overlap issue between primary S 2p and Si 2s in the spectrum, Sulphur content was characterized by S 2s in this study.)

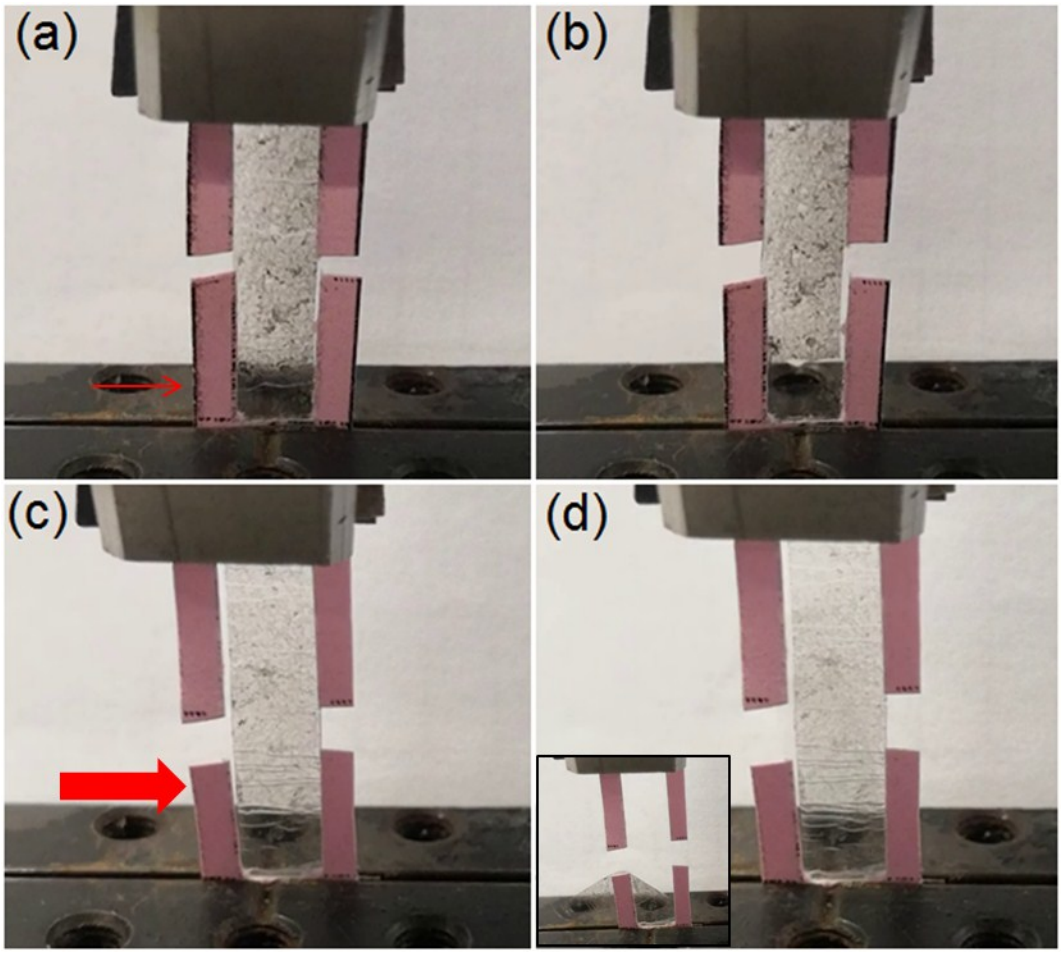

Figure S7: Demonstration of the elongated behaviours during the tensile test for covalent bonded bilayered composite and non-covalent bonded bilayered composite. (a) Stretching process for covalent bonded bilayered composite. Only one major crack happened on the rGO-chitosan-MA layer before the failure of whole composite. (b) The failure point of the covalent bonded bilayered composite. Composite crack went through the rGO-chitosan-MA layer crack. (c) Stretching process for non-covalent bonded bilayered composite. The rGO-chitosan-MA layer split into few parts before PDMS layer cracked. (d) The point before failure of the non-covalent bonded bilayered composite. (Inset: the failure point of the non-covalent bonded bilayered composite. The sample curled back and caused observation difficulty, so the point before failure was used for demonstration.)

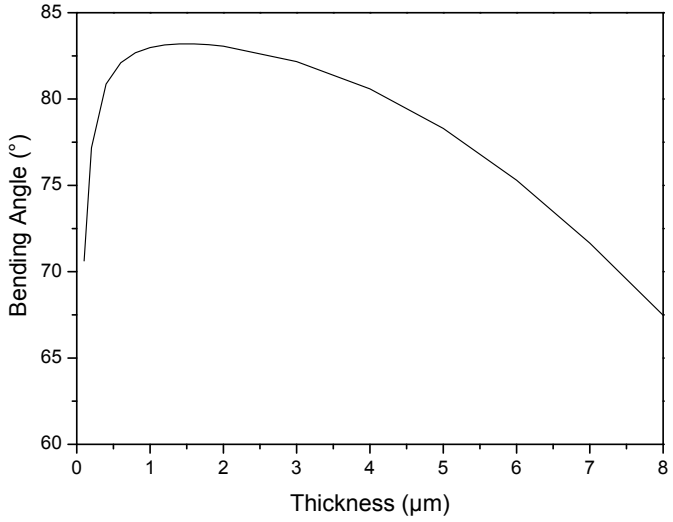

Figure S8: Relationship between the thickness of rGO-chitosan-MA layer and bending angle when PDMS thickness and temperature change remain the same on the basis of thermomechanics study of bimetallic thermostats in Equation (1).

REFERENCES

(1) Socrates, G. *Infrared Characteristic Group Frequencies:Tables and Charts*, Second Edi.; John Wiley & Sons, 1994.

(2) Valmikinathan, C. M.; Mukhatyar, V. J.; Jain, A.; Karumbaiah, L.; Dasari, M.; Bellamkonda, R. V. Photocrosslinkable Chitosan Based Hydrogels for Neural Tissue Engineering. *Soft Matter* **2012**, *8* (6), 1964–1976.

(3) Lavertu, M.; Xia, Z.; Serreqi, A. N.; Berrada, M.; Rodrigues, A.; Wang, D.; Buschmann, M. D.; Gupta, A. A Validated 1H NMR Method for the Determination of the Degree of Deacetylation of Chitosan. *J. Pharm. Biomed. Anal.* **2003**, *32* (6), 1149–1158.