

Supporting Information

# Exceptional Mechanical Properties of Phase-Separation-Free $\text{Mo}_3\text{Se}_3^-$ -Chain-Reinforced Hydrogel Prepared by Polymer Wrapping Process

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## Experimental Section

### *Chemicals and Materials*

In lump (99.99 %) was purchased from Kojundo (Chemical Laboratory, Saitama, Japan). Mo powder ( $\geq 99.9$  %) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Se powder (99 %+), LiI (99.999 %) powder and Amberlite IR-120H resin for ion exchange was purchased from Alfa Aesar (Ward Hill, MA). Gelatin type A (300 g Bloom) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Deionized water (18.2 M $\Omega$  cm) was prepared using a Sartorius Arium®Pro Ultrapure water system. All the reagents were used without further purification.

### *Preparation of LiMo<sub>3</sub>Se<sub>3</sub> sample:*

LiMo<sub>3</sub>Se<sub>3</sub> was synthesized by an ion exchange reaction between InMo<sub>3</sub>Se<sub>3</sub> and LiI. The starting material, InMo<sub>3</sub>Se<sub>3</sub>, was prepared by a solid-state reaction using In lump, Mo powder, and Se powder. The stoichiometric amount of each elements was mixed, and then pelletized. The pellet was sealed in an evacuated quartz tube, and the tube was heated to 1050 °C for 48 h (at 100 °C h<sup>-1</sup>). Then, as-prepared InMo<sub>3</sub>Se<sub>3</sub> was pelletized with stoichiometric amount of LiI (In Mo<sub>3</sub>Se<sub>3</sub>/LiI = 1:1) in Ar atmosphere glovebox, and the pellet was sealed in a 30 cm long quartz tube. A sealed quartz tube was placed inside the tube furnace. Next, the reactant was heated, first rapidly to 370 °C, and then slowly to 550 °C (at 3 °C h<sup>-1</sup>), while the other side was maintained at room temperature. These temperatures were maintained for 96 h. In the hot-zone, In ions of InMo<sub>3</sub>Se<sub>3</sub> were exchanged with Li ions of LiI via a substitution reaction. The substituted InI, and the excess LiI were deposited on the low-temperature regions of the tube.

### *Preparation of aqueous Mo<sub>3</sub>Se<sub>3</sub><sup>-</sup> solution:*

The aqueous Mo<sub>3</sub>Se<sub>3</sub><sup>-</sup> solution are prepared as previously reported.<sup>1</sup> The as-prepared Li Mo<sub>3</sub>Se<sub>3</sub> was ultrasonicated for 30 min in DI water with the concentration of 0.5 mg/mL. After that, the solution was centrifuged at 12,298 rcf for 10 min to remove insufficiently dispersed wires and then supernatant solutions were used for Li ion exchange. An ion-exchange resin (Amberlite IR-120H) was washed several times with DI water. The exchange resin was suspended in water, and the chromatography column were filled with the resin. The DI water level was set so that

all the resins were submerged. The supernatant solution was passed through the ion exchange resin to remove the Li cations in air atmosphere. Finally, the aqueous  $\text{Mo}_3\text{Se}_3^-$  solutions after ion exchange are used for the preparation of  $\text{Mo}_3\text{Se}_3^-$  reinforced gelatin hydrogel.

*Preparation of composite hydrogel by simple mixing:*

The composite hydrogel was prepared by simply mixing gelatin type A with various concentrations (0, 0.003, 0.01, and 0.05 wt%) of  $\text{Mo}_3\text{Se}_3^-$  chain nanowire. Final concentration of gelatin used in each composite hydrogel was 15 wt%. After heating over 70 °C, the mixed solution was poured into a mold and cooled down to 4 °C.

*Preparation of composite hydrogel by polymer wrapping method:*

To find the appropriate wrapping ratio between gelatin and  $\text{Mo}_3\text{Se}_3^-$  chain nanowire, a solution containing various concentrations of gelatin polymer (20 mL; 0, 0.02, 0.06, 0.1, 0.2, 0.5, 1, and 2 wt%) was poured to  $\text{Mo}_3\text{Se}_3^-$  nanowire solution (20 mL and 0.02 wt%). The solution containing both gelatin and  $\text{Mo}_3\text{Se}_3^-$  chain nanowire was then ultrasonicated for about 30 min and then shaken for 90 min with a constant stirring at 400 rpm. After adding additional gelatin powder into the solution containing gelatin wrapped  $\text{Mo}_3\text{Se}_3^-$  nanowire, the mixed solution was heated at 70 °C, poured into a mold, and cooled down to 4 °C. The final gelatin concentration in each composite hydrogel sample was 15 wt%. Because the tensile strength and fracture strain of the composite hydrogel had maximum values when gelatin /  $\text{Mo}_3\text{Se}_3^-$  was 25, this condition was used for most experiments.

*Zeta potential measurement:*

We used Malvern Zetasizer Nano-ZS90 (UK) with 4 mW He-Ne laser operating at 633 nm for Dynamic Light Scattering (DLS measurement). DLS measurements were performed with triplicate samples and error bar indicates stand deviation of the measurement. The instrument was standardized prior to each experiment following calibration standards.

*Tensile strength measurement:*

The tensile strength of gelatin and composite hydrogels were measured via tensile testing (Comtech, QC-508E) using a 100 kgf load cell with  $10 \text{ mm} \cdot \text{min}^{-1}$  loading speed. Five samples were measured in each condition at room temperature. The width and thickness of each sample was 3 mm and 10 mm, respectively.

*Stability test:*

To test the stability of our composite hydrogel, we measured tensile strength of the composite hydrogels stored for 1 to 5 days both at room temperature and in a refrigerated condition ( $4 \text{ }^\circ\text{C}$ ). Small amount of water was added on the composite hydrogels while storage to prevent them from being dried.

*SEM measurement:*

The microstructure of each sample was observed using a scanning electron microscope (SEM, Hitachi S-4800). The hydrogel samples were freeze-dried at  $-70 \text{ }^\circ\text{C}$  (FD 8508, Ilshin Biobase Co. Ltd, Dongduchun, Korea) to minimize their morphological changes.<sup>2,3</sup> All the freeze-dried hydrogel samples were coated with Pt before imaging.

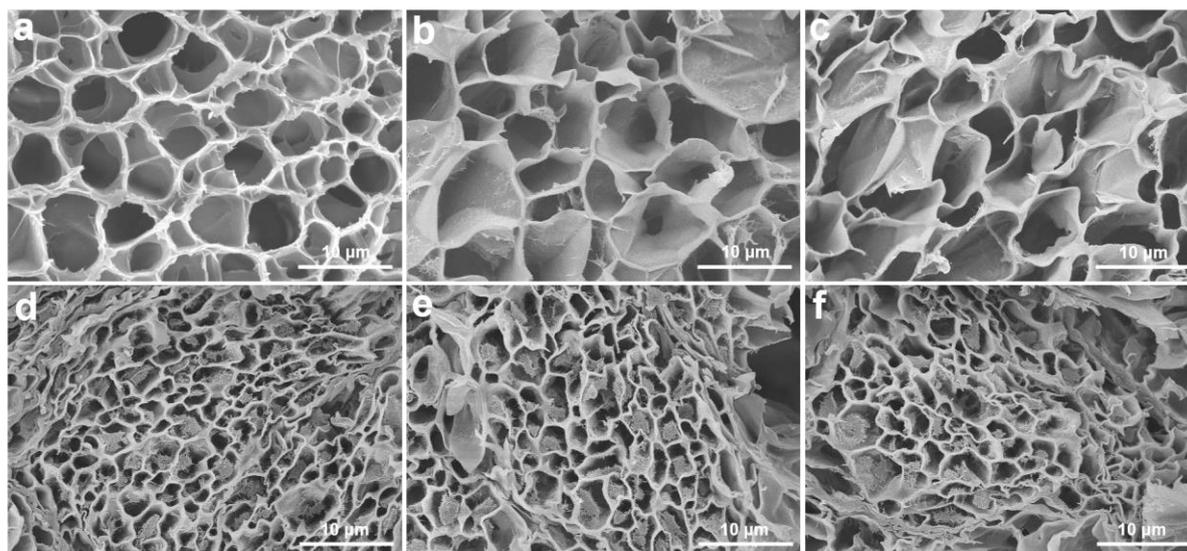
*TEM measurement:*

In order to image bare  $\text{Mo}_3\text{Se}_3^-$  nanowires and gelatin wrapped nanowires using transmission electron microscope (TEM), lacey carbon TEM grid (300 mesh Cu lacey carbon) was used. Each sample (13  $\mu\text{L}$ ) was dropped on the grids and dried for 2 h. Bare and gelatin wrapped  $\text{Mo}_3\text{Se}_3^-$  nanowires were analyzed with TEM (JEM-2100F) operated at 200 kV.

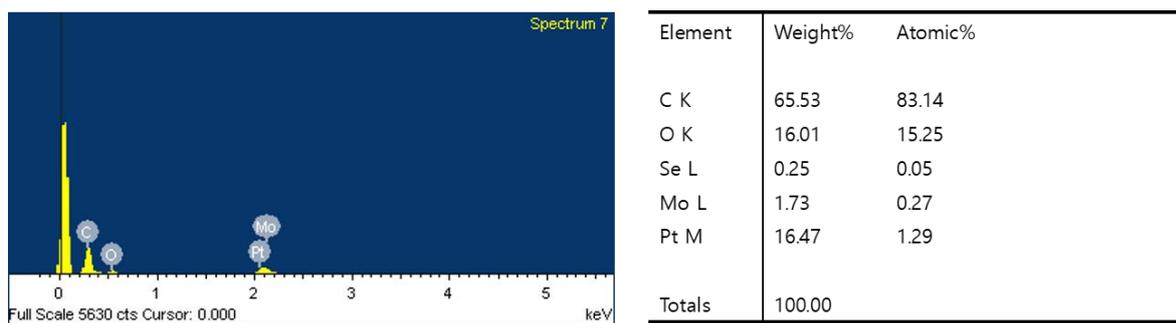
## Supporting Figures

**Table S1.** ICP-MS result of  $\text{LiMo}_3\text{Se}_3$  aqueous solution.

	<b>In to Li ratio</b>
$\text{LiMo}_3\text{Se}_3$ aqueous solution	1.5 : 98.5



**Figure S1.** Cross section SEM images of (a-c) pure gelatin and (d-f) composite hydrogels.



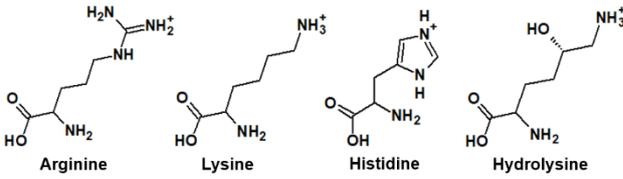
**Figure S2.** Energy dispersive X-ray (EDX) analysis spectra of composite hydrogel.

**Table S2.** Amino acids present in type A gelatin.

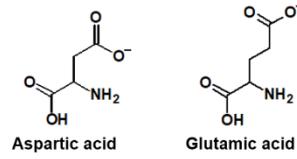
<b>Amino acid</b>	<b>Property</b>	<b>wt%</b>
Glycine	Non polar	23.6
Proline	Non polar	14.5
Hydroxyproline	Non polar	12.1
Glutamic acid	Polar, negative	10.1
Alanine	Non polar	7.7
*Arginine	Polar, positive	7.4
Aspartic acid	Polar, negative	5.5
*Lysine	Polar, positive	3.7
Leucine	Non polar	2.8
Serine	Polar, neutral	2.6
Valine	Non polar	2.2
Threonine	Polar, neutral	2.0
Phenylalanine	Non polar	1.9
Isoleucine	Non polar	1.3
*Hydroxylysine	Polar, positive	0.9
Methionine	Non polar	0.7
*Histidine	Polar, positive	0.8
Tyrosine	Polar, neutral	0.4
Cystine	Polar, neutral	0.1
Total	-	100

\* Amino acids with positive charges.

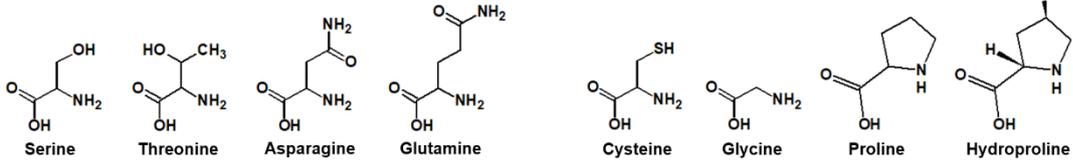
**Positive charged amino acid**



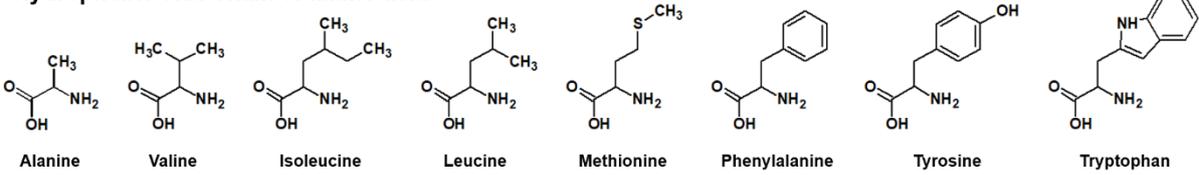
**Negative charged amino acid**



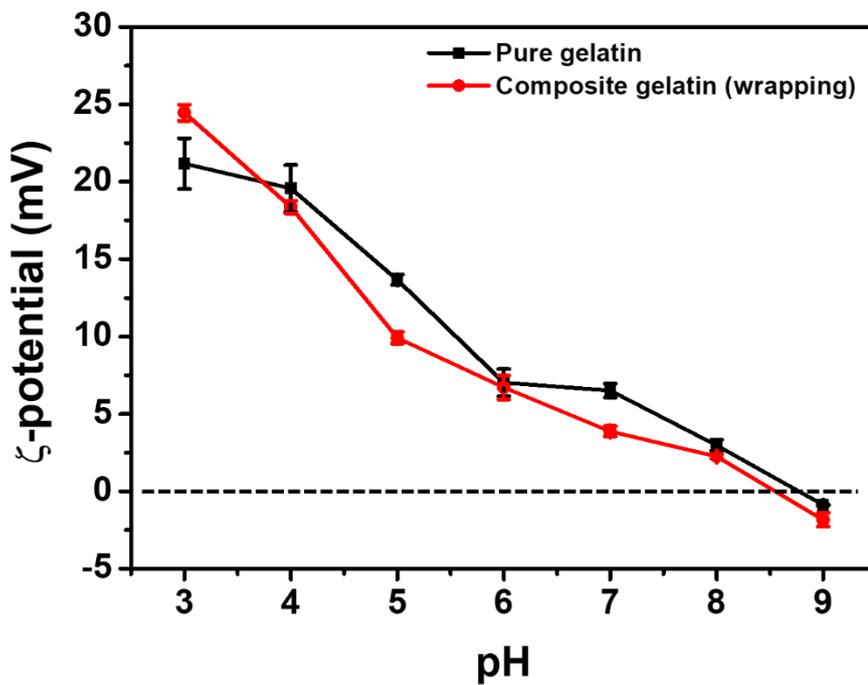
**Polar uncharged amino acid**



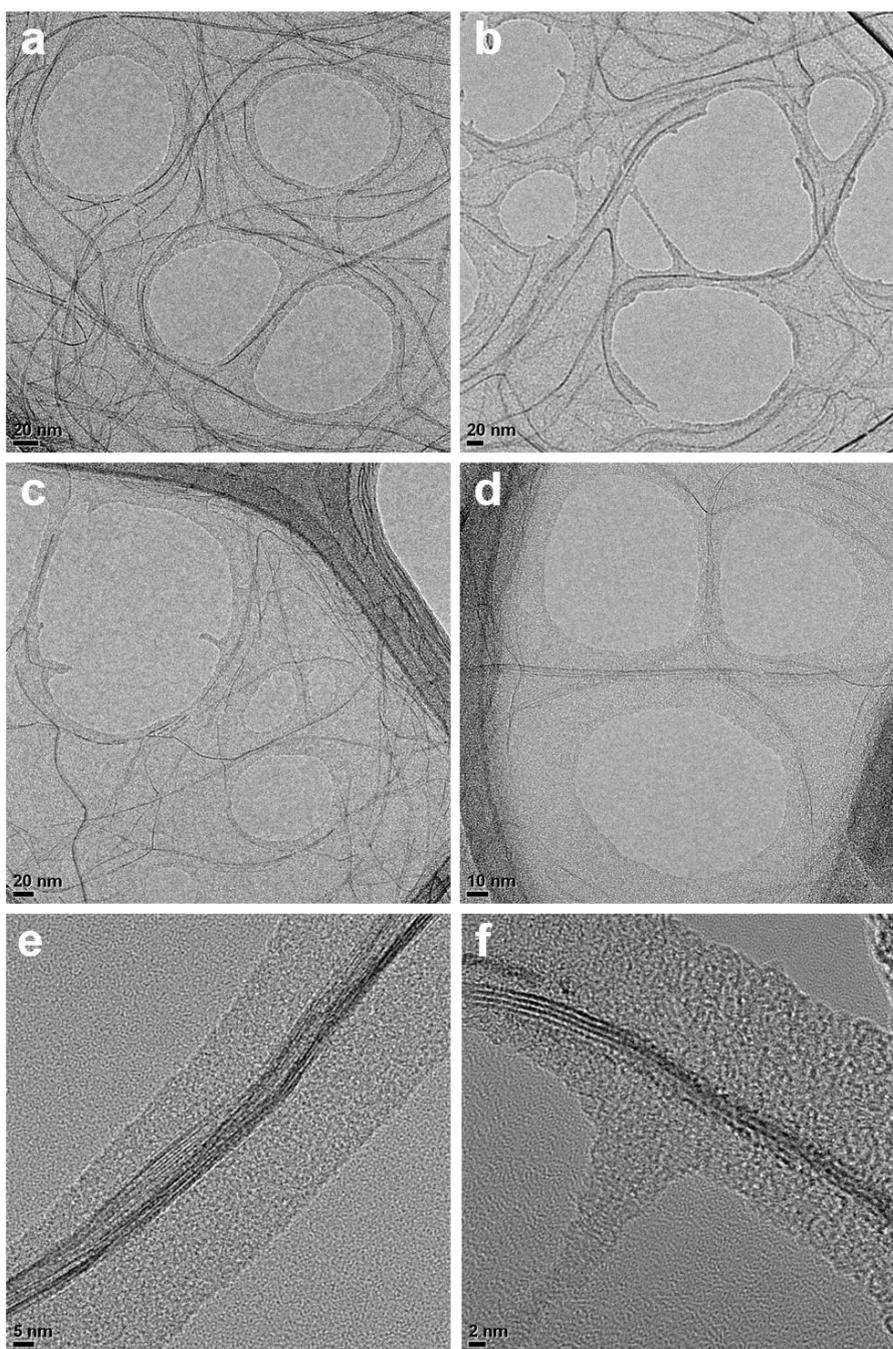
**Hydrophobic side chain of amino acid**



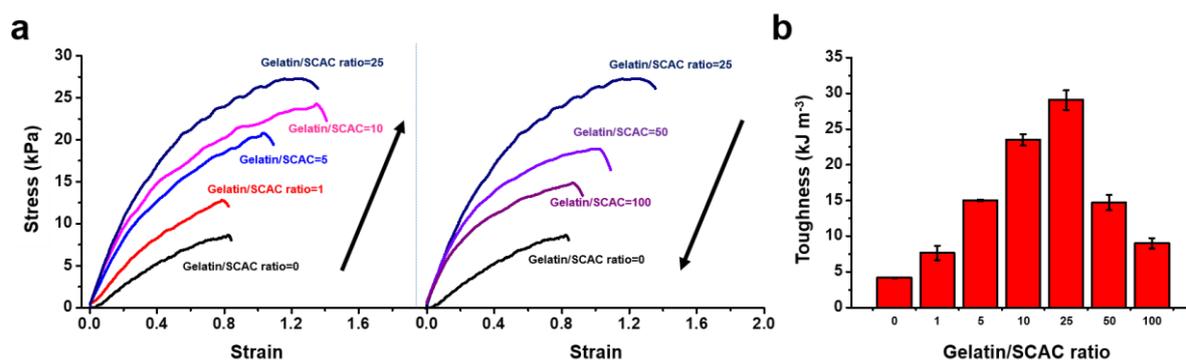
**Figure S3.** Structures of amino acid present in type A gelatin.



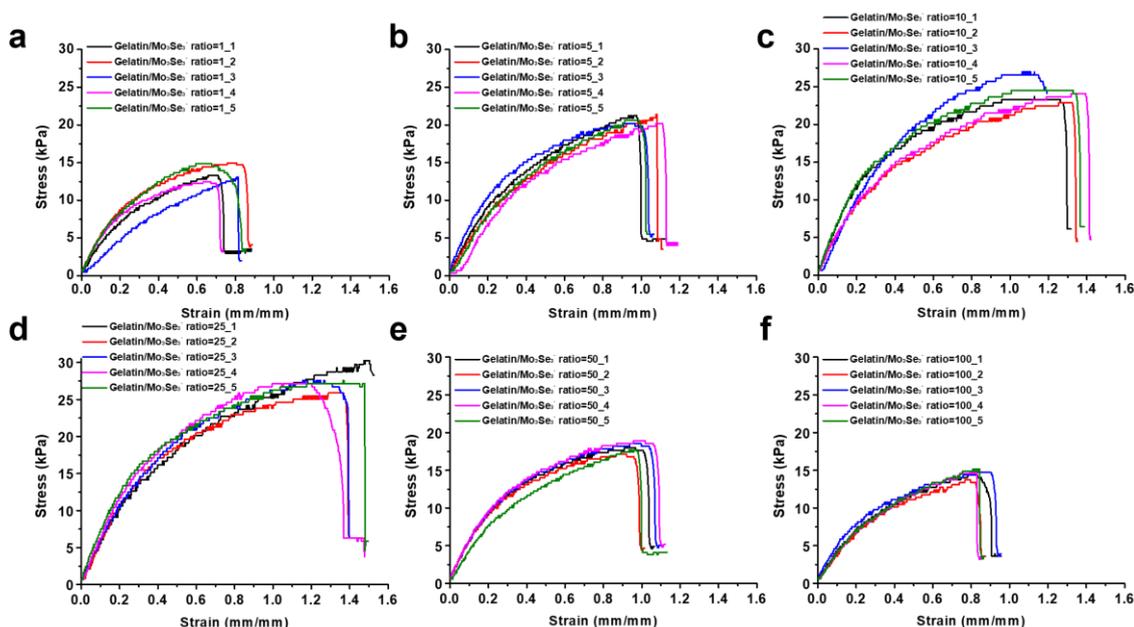
**Figure S4.** Comparison of zeta potential values of pure gelatin (black) and gelatin wrapped  $\text{Mo}_3\text{Se}_3^-$  nanowires (red) measured in the different pH conditions.



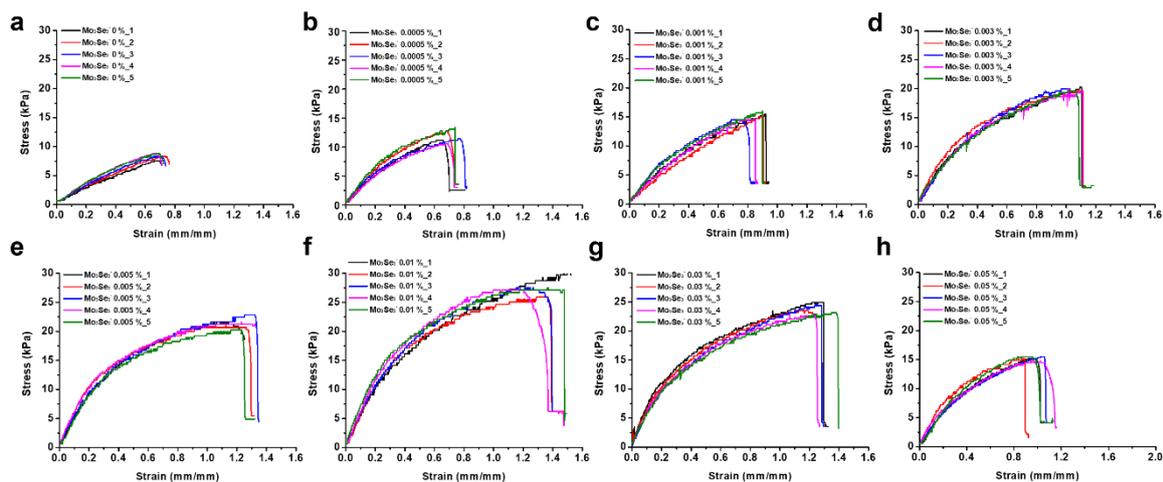
**Figure S5.** TEM images of gelatin wrapped  $\text{Mo}_3\text{Se}_3$  nanowires prepared with gelatin/SCAC ratio of 25. (a-d) low magnified and (e,f) high magnified images.



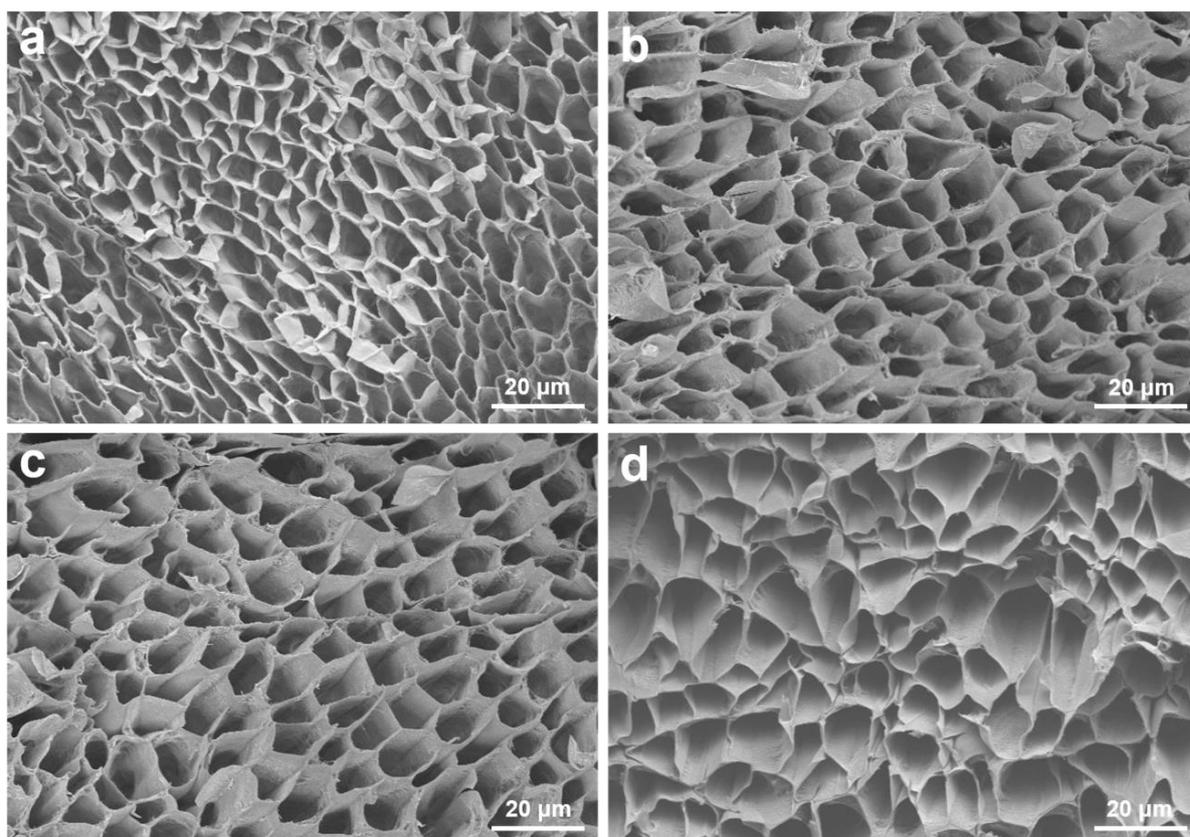
**Figure S6.** The mechanical properties of composite hydrogels prepared by wrapping method in different gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio. (a) Stress-strain curve and (b) toughness



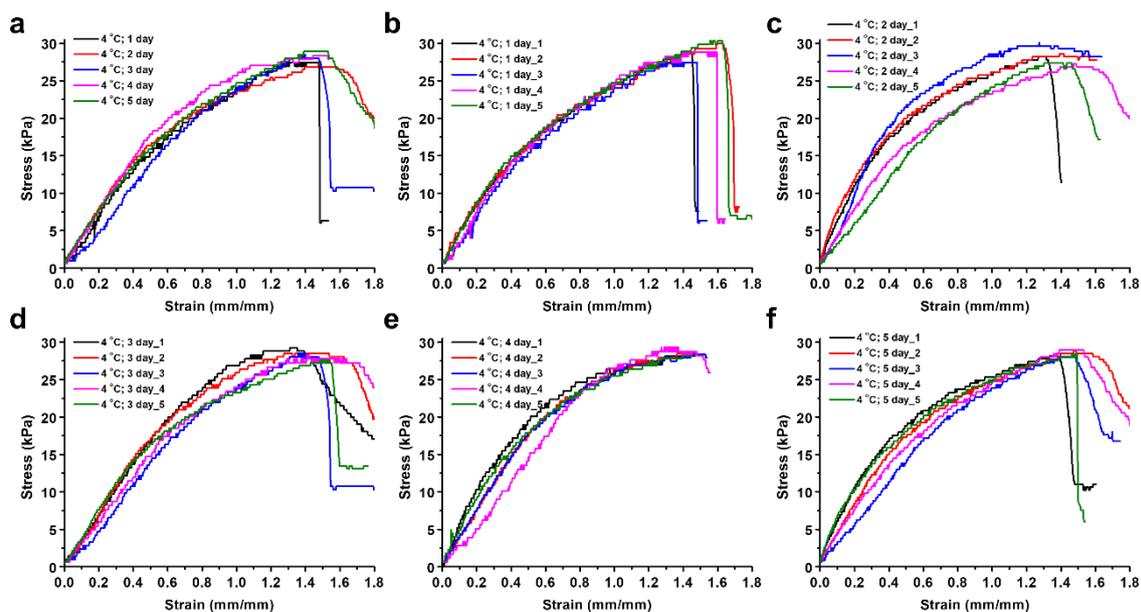
**Figure S7.** The mechanical properties of composite hydrogels with different gelatin/ $\text{Mo}_3\text{Se}_3^-$  ratios. Composite hydrogel prepared at each condition was tested 5 times. (a) Gelatin/ $\text{Mo}_3\text{Se}_3^-$  ratio=1, (b) gelatin/ $\text{Mo}_3\text{Se}_3^-$  ratio=5, (c) gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio=10, (d) gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio=25, (e) gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio= 50, and (f) gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio=100.



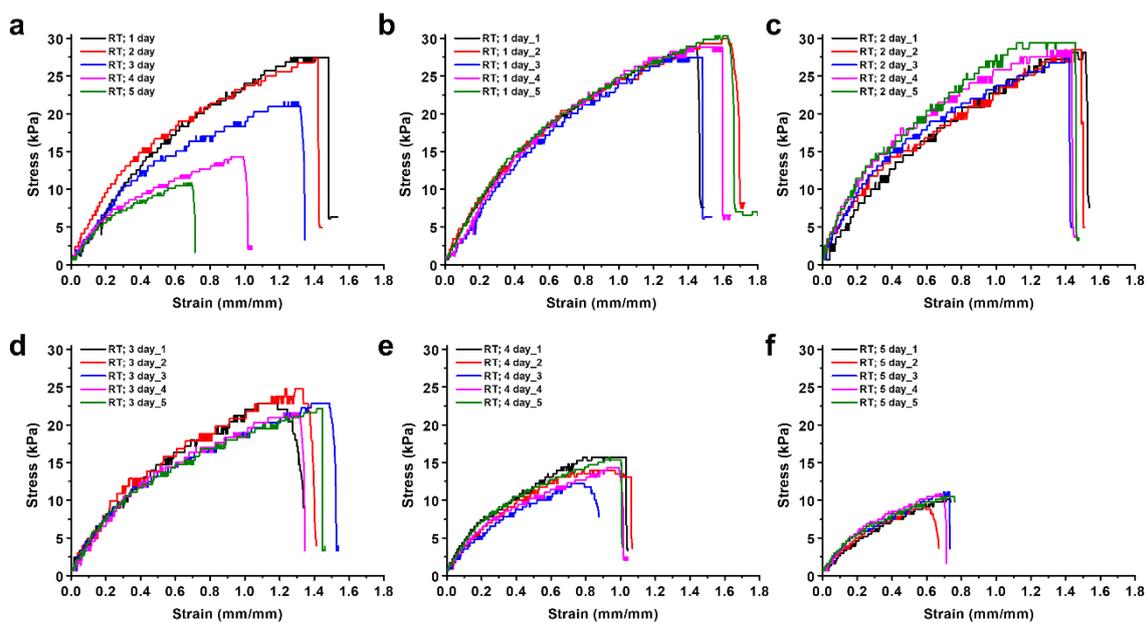
**Figure S8.** The mechanical properties of composite hydrogels containing different concentrations of  $\text{Mo}_3\text{Se}_3^-$  nanowire. Gelatin/ $\text{Mo}_3\text{Se}_3^-$  ratio was fixed to 25. Composite hydrogel prepared at each condition was tested 5 times. (a)  $\text{Mo}_3\text{Se}_3^-$  0 %, (b)  $\text{Mo}_3\text{Se}_3^-$  0.0005%, (c)  $\text{Mo}_3\text{Se}_3^-$  0.001 %, (d)  $\text{Mo}_3\text{Se}_3^-$  0.003 %, (e)  $\text{Mo}_3\text{Se}_3^-$  0.005 %, (f)  $\text{Mo}_3\text{Se}_3^-$  0.01 %, (g)  $\text{Mo}_3\text{Se}_3^-$  0.03 %, and (h)  $\text{Mo}_3\text{Se}_3^-$  0.05 %.



**Figure S9.** SEM images of composite hydrogels. All the images were taken from different samples prepared in identical condition with 0.01 wt % of  $\text{Mo}_3\text{Se}_3^-$  nanowire. Gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio was fixed to 25 and the final concentration of gelatin is identical (15 wt%).



**Figure S10.** The stability of composite hydrogel stored at 4 °C condition for 1-5 days before testing. Composite hydrogel prepared at each condition was tested 5 times. Gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio was fixed to 25. (a) Variation of stress-strain curves of samples stored for 1 to 5 days. (b-f) Stress-strain curves of samples stored for (b) 1 day, (c) 2 days, (d) 3 days, (e) 4 days, and (f) 5 days.



**Figure S11.** The stability of composite hydrogel stored at room temperature for 1-5 days before testing.

testing. Composite hydrogel prepared at each condition was tested 5 times. Gelatin/  $\text{Mo}_3\text{Se}_3^-$  ratio was fixed to 25. (a) Variation of stress-strain curves of samples stored for 1 to 5 days. (b-f) Stress-strain curves of samples stored for (b) 1 day, (c) 2 days, (d) 3 days, (e) 4 days, and (f) 5 days.

## REFERENCES

1. Chae, S.; Oh, S.; Siddiqa, A. J.; Choi, K. H.; Lee, W.-G.; Jang, W.-S.; Lee, J. S.; Kim, Y.-M.; Huh, J.; Kim, S. M., Choi, J.-Y. *Chem. Commun.* **2018**, 54 (88), 12503-12506.
2. Simoni, R. C.; Lemes, G. F.; Fialho, S.; Goncalves, O. H.; Gozzo, A. M.; Chiaradia, V.; Sayer, C; Shirai, M. A.; Leimann, F. V. *An. Acad. Bras. Ciênc.* **2017**, 89 (1), 745-755.
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