

Supporting Information

Preferential Interfacial Engineering of Hydrogels via Interdigitated Nanoparticle Assembly

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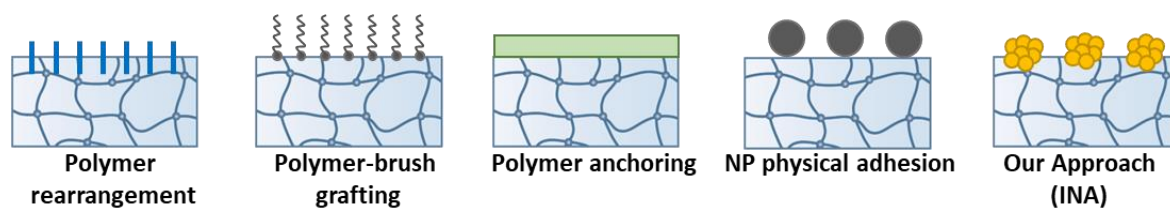


Figure S1. Schematic illustration of previous approaches (i.e., polymer rearrangement, polymer-brush grafting, polymer coating, NP physical adhesion) for the interfacial engineering of hydrogels and our approach (interdigitated nanoparticle assembly, INA).

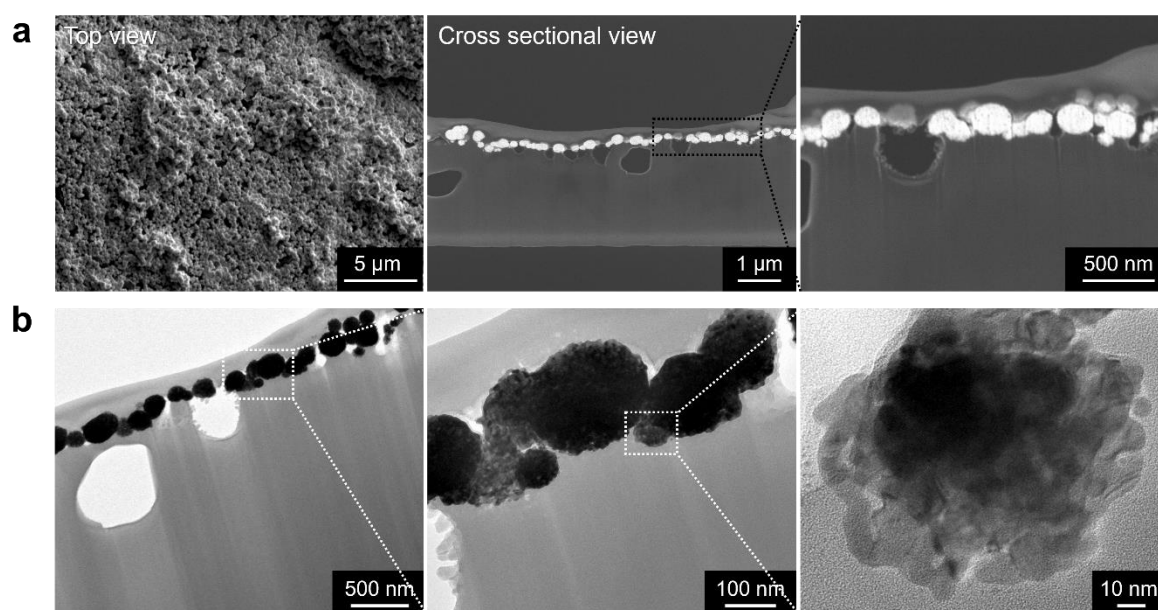


Figure S3. (a) Top and cross-sectional FIB-SEM and (b) cross-sectional HR-TEM images of INA-hydrogel (immersion time: 10 min).

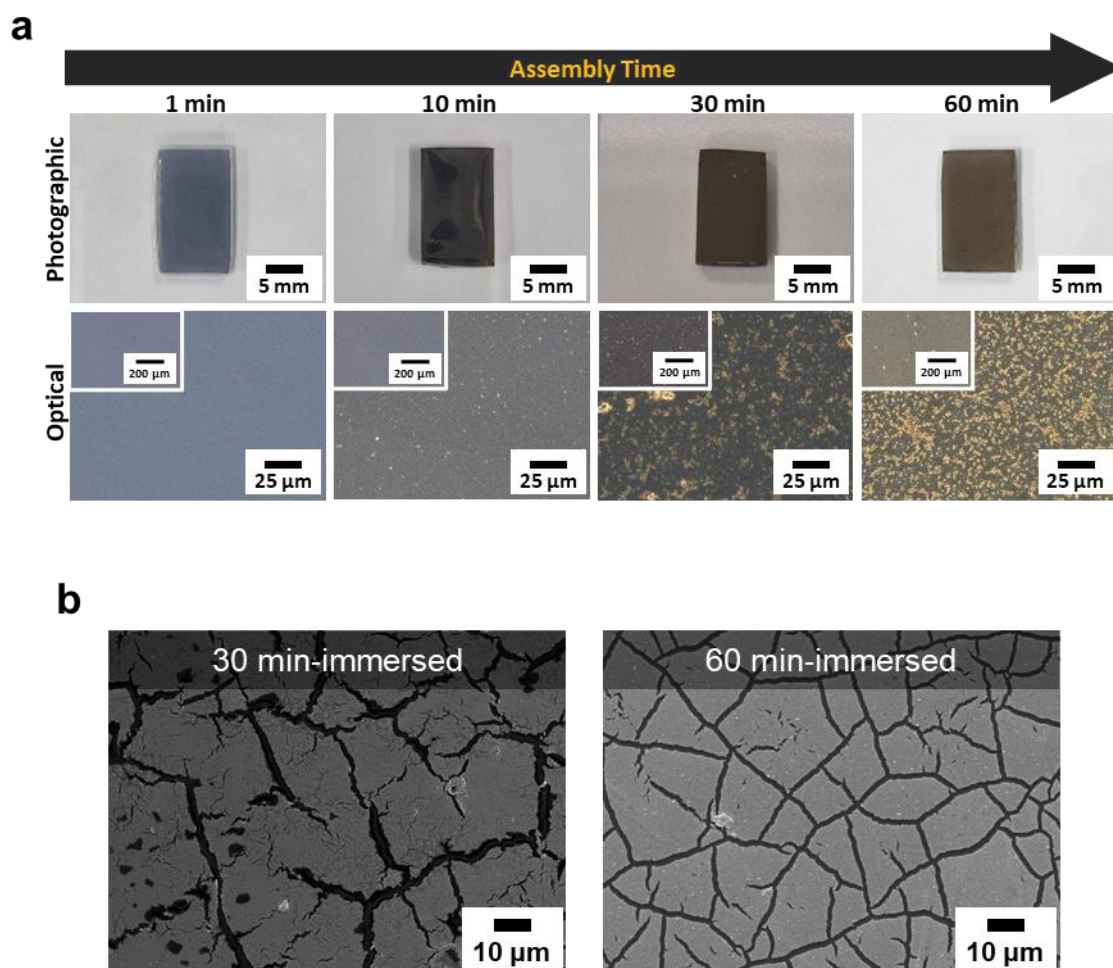


Figure S4. (a) Time-dependent assembly of AuNPs on the hydrogel surface. The top row displays photographic images. The bottom row shows optical microscopy images at 1000× (with 100× insert views). (b) SEM images of INA-hydrogels after immersion for 30 and 60 min.

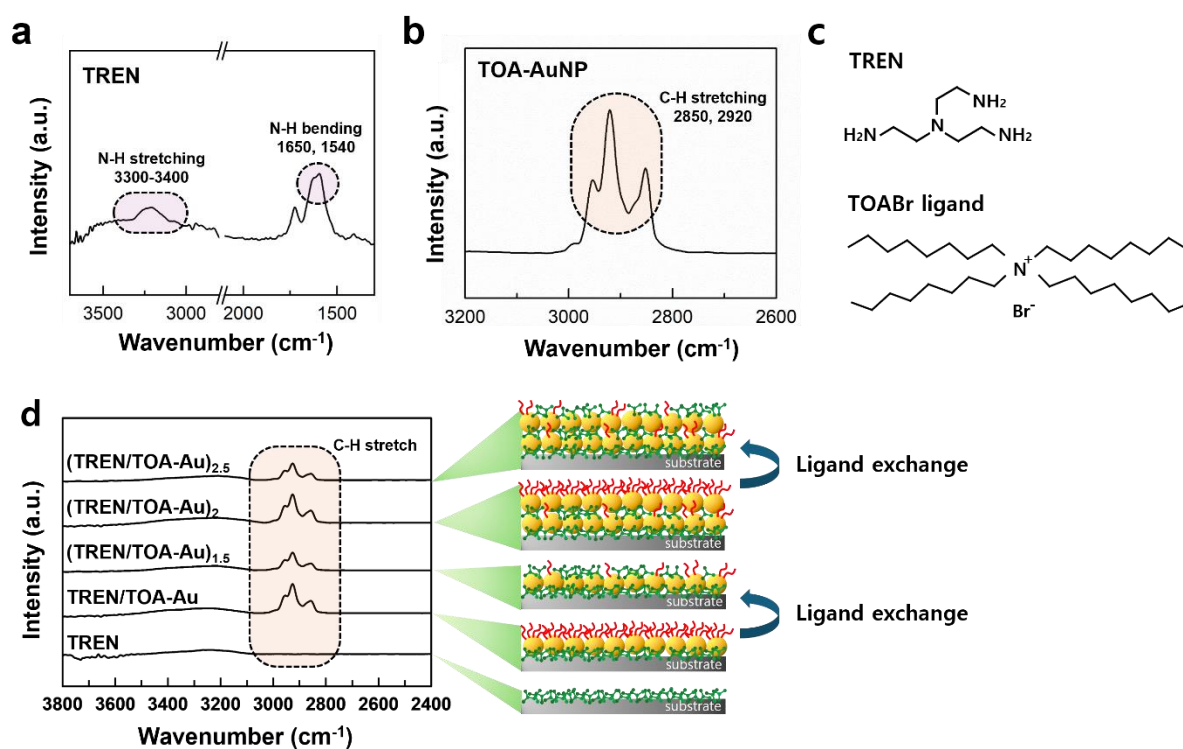


Figure S5. FT-IR spectra of (a) pristine TREN and (b) pristine tetraoctylammonium (TOA) – AuNPs. (c) Chemical structures of TREN and TOABr. (d) FTIR spectra and scheme of the LbL-assembled multilayers (TREN/TOA-AuNP)_{*n*} as a function of the bilayer number (*n*).

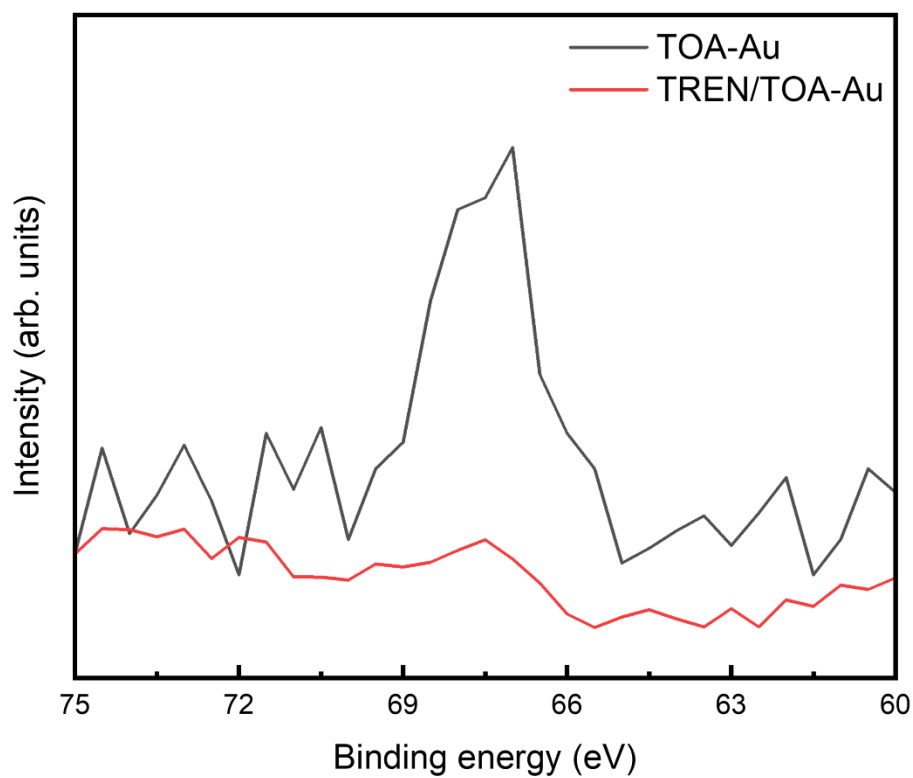


Figure S6. Typical Br3d XPS spectra of the pristine tetraoctylammonium (TOA)–AuNPs and the TREN treated TOA–AuNPs prepared by drop-casting on wafer.

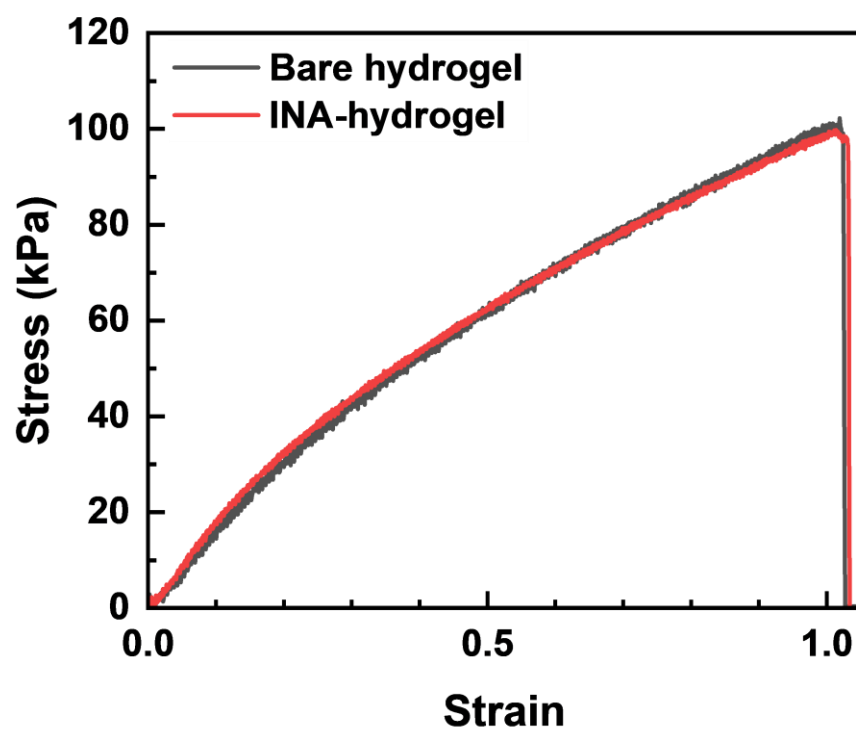


Figure S7. Stress–strain curves of the bare hydrogel and the INA-hydrogel.

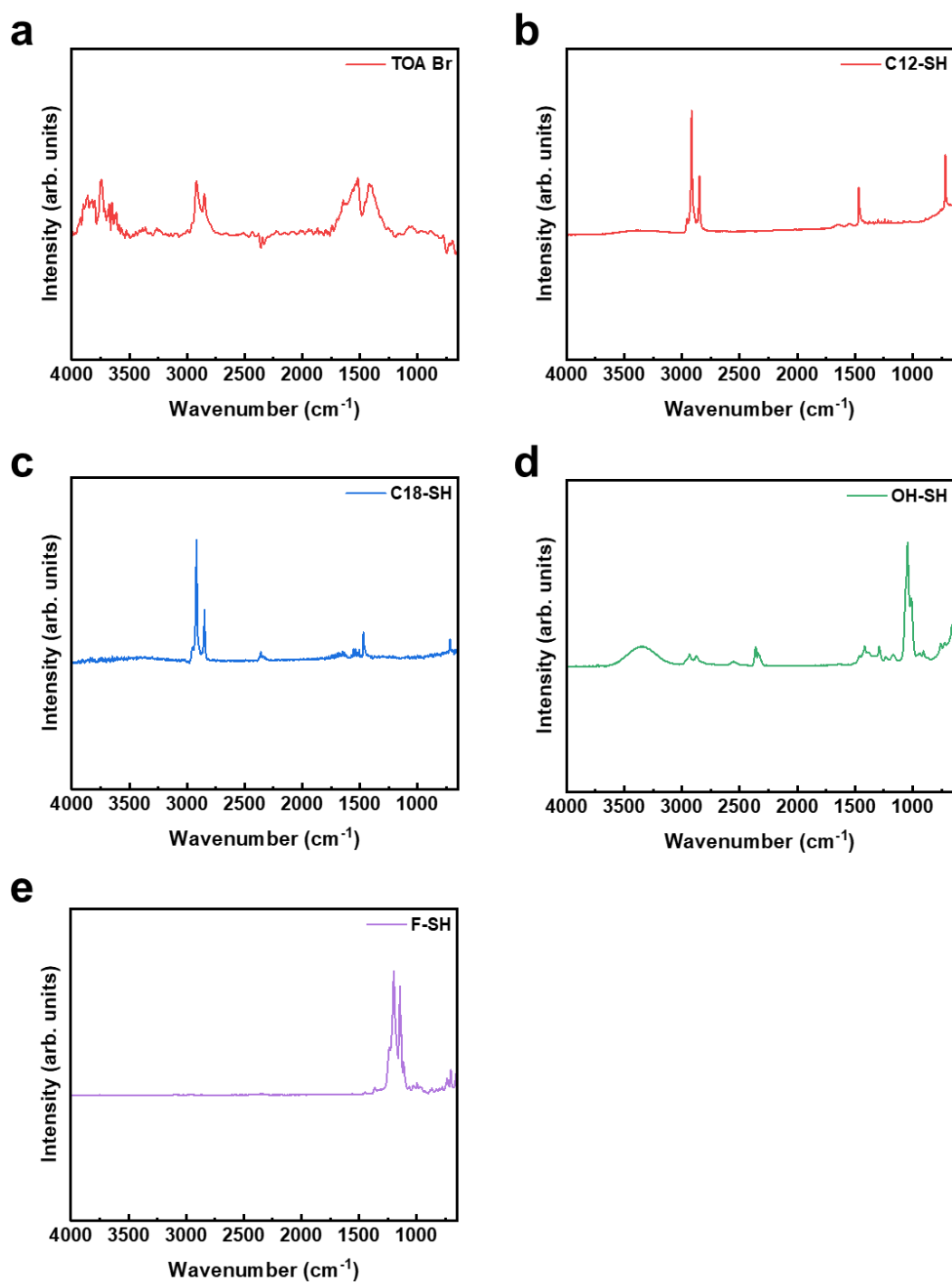


Figure S8. FT-IR spectra of (a) TOA, (b) 1-dodecanethiol (C12-SH), (c) 1-octadecanethiol (C18-SH), (d) 2-mercaptoethanol (OH-SH), and (e) 1H,1H,2H,2H-perfluorodecanethiol (F-SH) small molecule linkers.

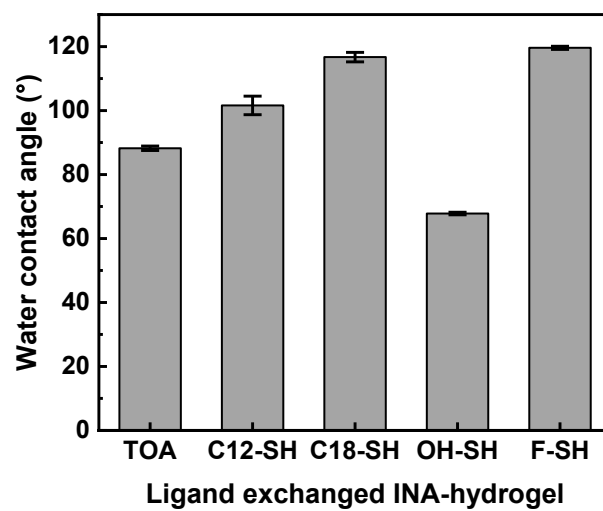


Figure S9. Static water contact angles measured on INA-hydrogel (immersion time: 10 min) after treating small molecule linkers.

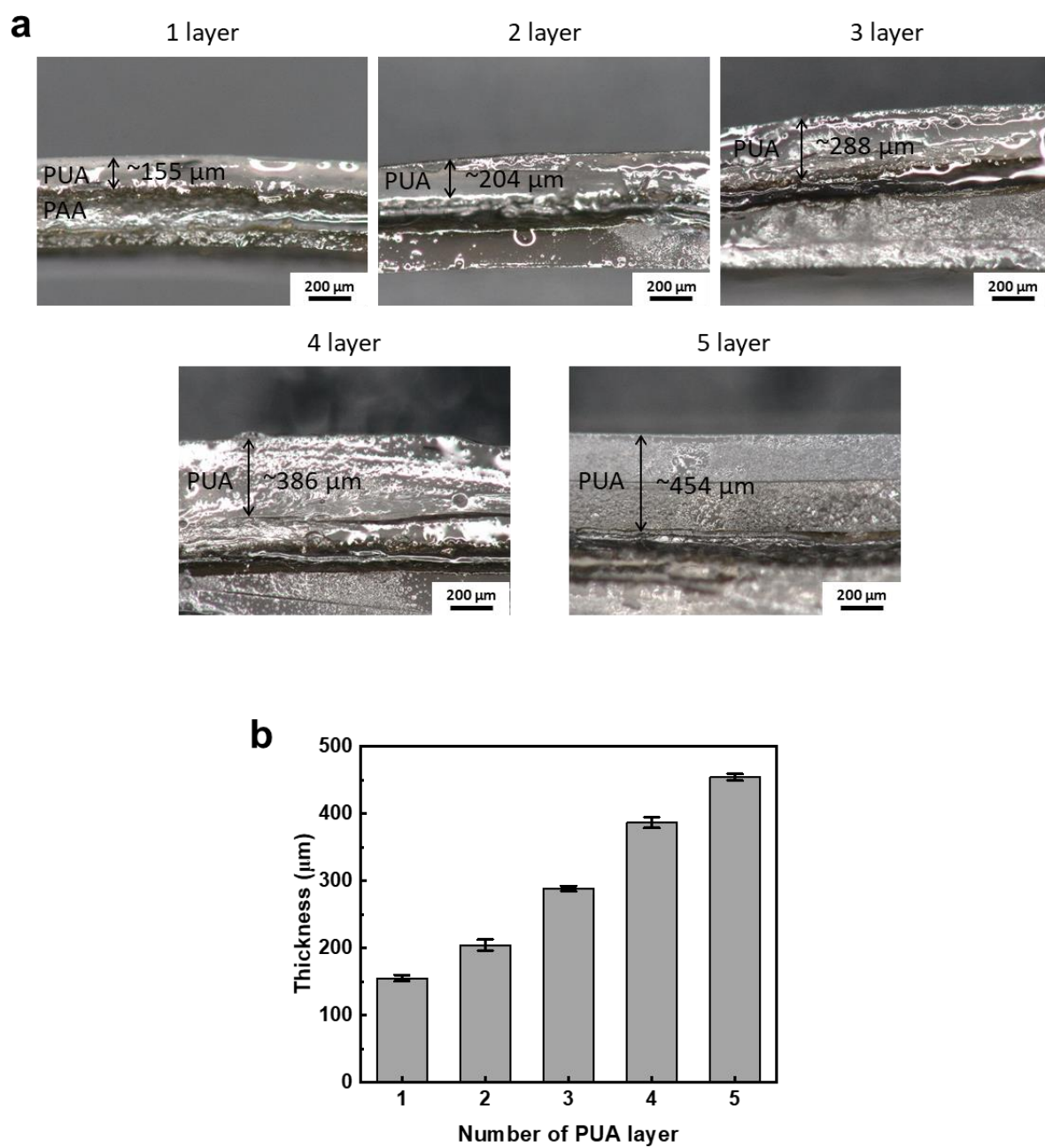


Figure S10. (a) Cross-sectional optical microscopy (OM) images of poly(urethane acrylate) (PUA) layers deposited on INA-hydrogel surfaces with varying thicknesses. (b) Change in PUA coating thickness on INA-hydrogels as a function of the number of deposited layers.

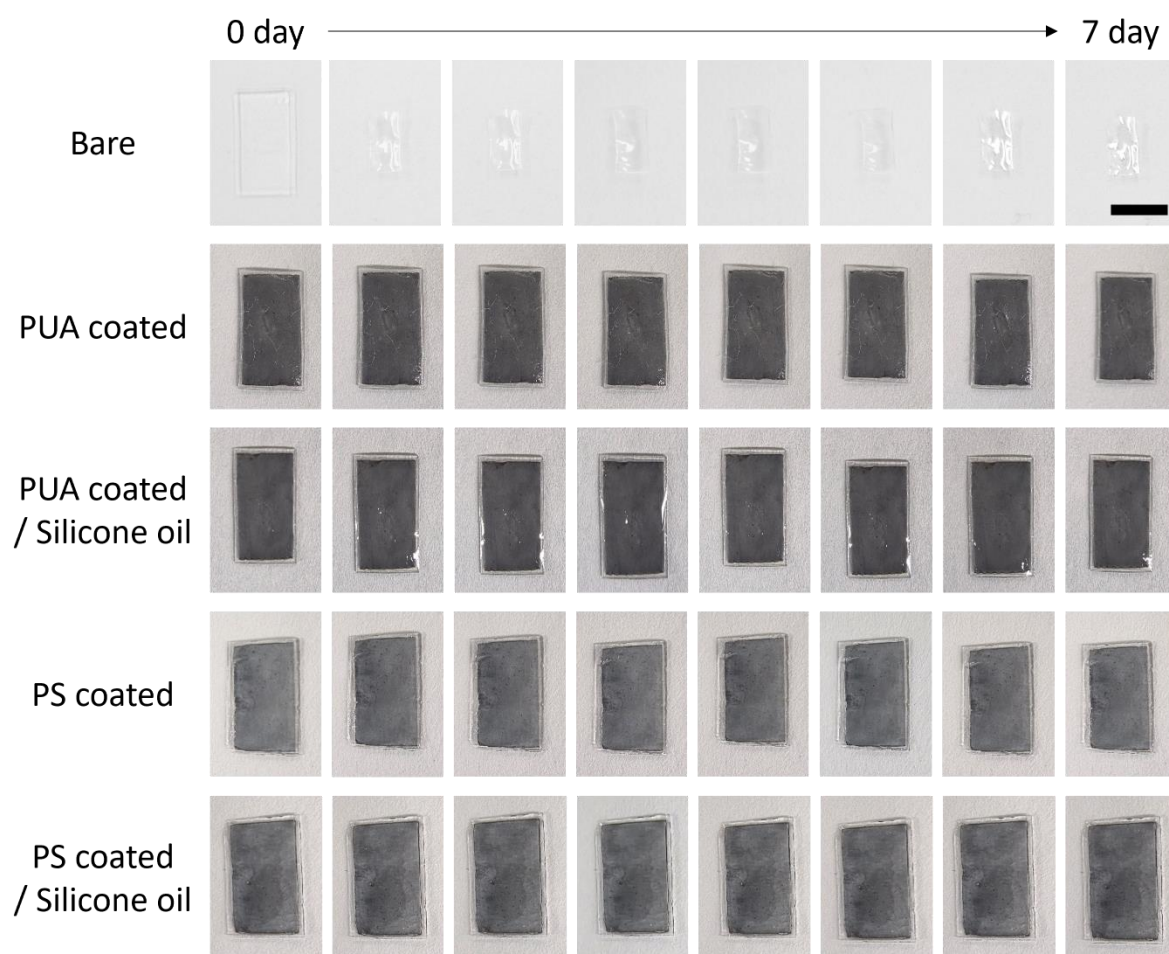


Figure S11. Photographic images of bare, PUA deposited, silicone oil infused PUA deposited, polysiloxane (PSO) deposited, and silicone oil infused PSO deposited hydrogels over 7 days (scale bar : 1 cm)

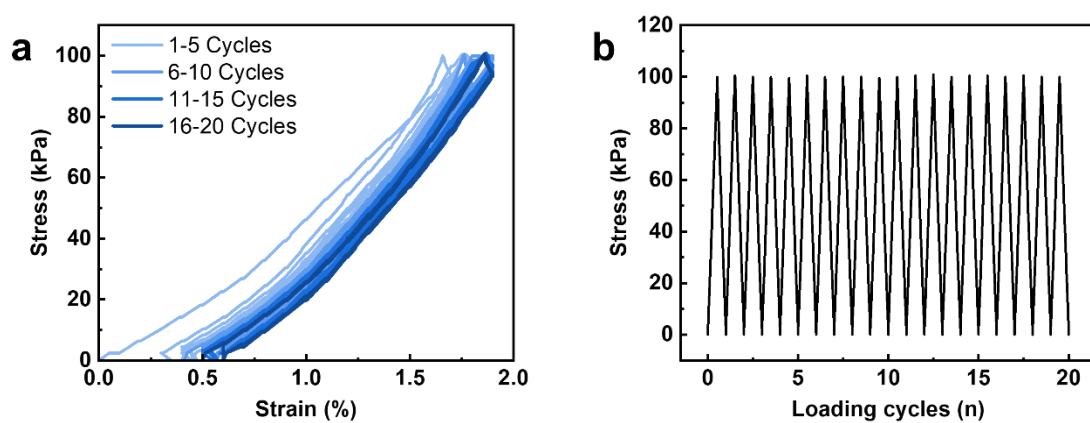


Figure S12. (a) Stress–strain curves and (b) stress-loading cycles obtained from cycle loading tests of cyanocrylate-based bioadhesive-treated INA-hydrogel.

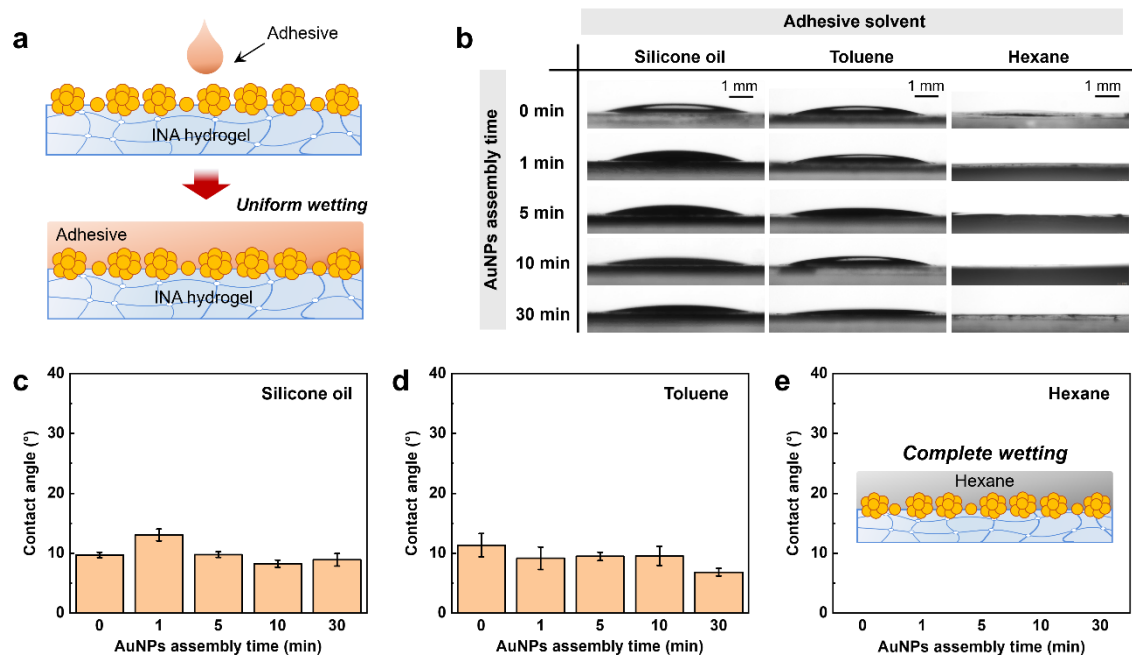


Figure S13. (a) Schematic illustration of adhesive wetting on INA-hydrogels. (b) Droplet images of non-polar liquids (*n*-hexane, toluene, and silicone oil) on bare (0 min) and INA-hydrogels fabricated with different AuNPs assembly times. (c-e) Static contact angles of (c) *n*-hexane, (d) toluene, and (e) silicone oil on bare and INA-hydrogels as a function of immersion time fabricated with different AuNPs assembly times.

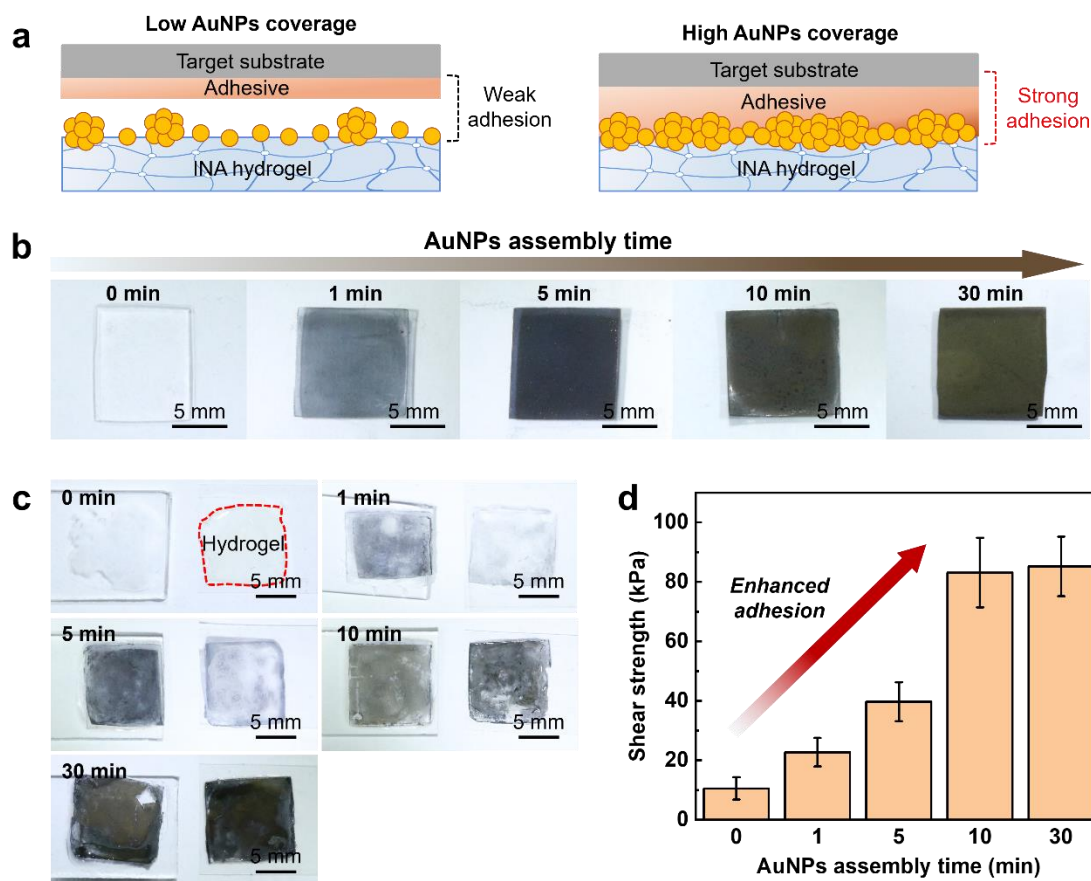


Figure S14. (a) Schematic illustration of AuNPs coverage dependent adhesion strength between INA-hydrogels and target substrates. (b-c) Photographic images of bare and INA-hydrogels fabricated with different AuNPs assembly times (b) before and (c) after lap-shear tests using cyanoacrylate-based bioadhesive. (d) Shear strengths of cyanoacrylate-based bioadhesive-treated bare and INA-hydrogels obtained from lab-shear tests.

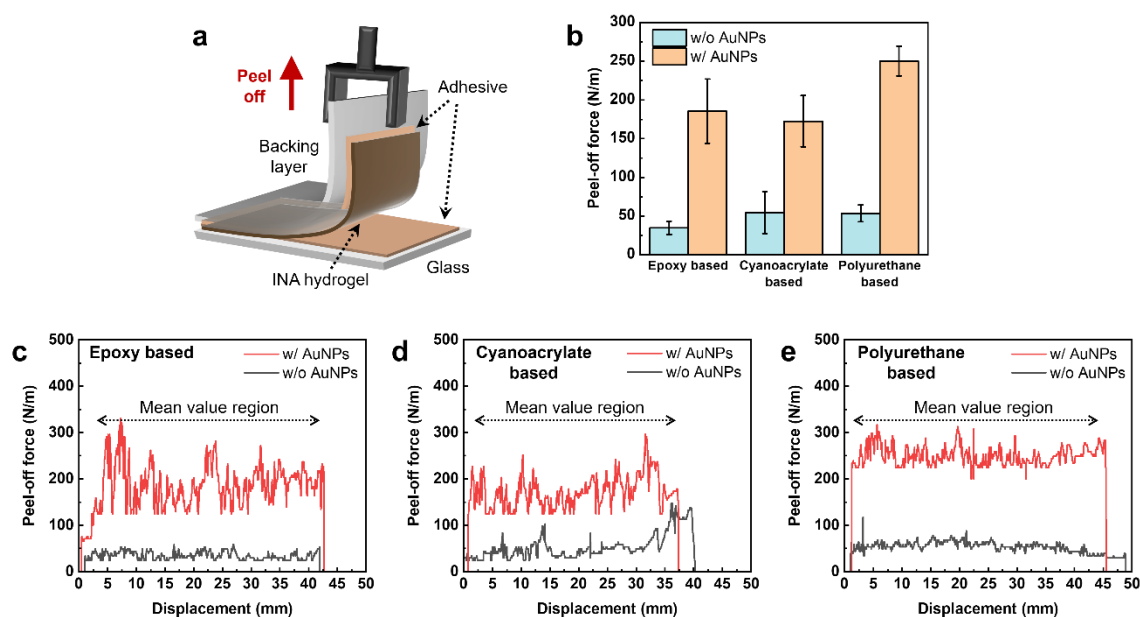


Figure S15. (a) Schematic illustration of peel-off test of bioadhesive-treated INA-hydrogel bonded to substrate. (b) Adhesion forces of INA-hydrogels measured obtained from peel-off tests using different commercial adhesives, including epoxy-, cyanoacrylate-, and polyurethane-based systems. (c-e) Force-displacement curves obtained from peel-off tests of bare hydrogels and INA-hydrogels treated with (c) epoxy-, (d) cyanoacrylate-, and (e) polyurethane-based adhesives.

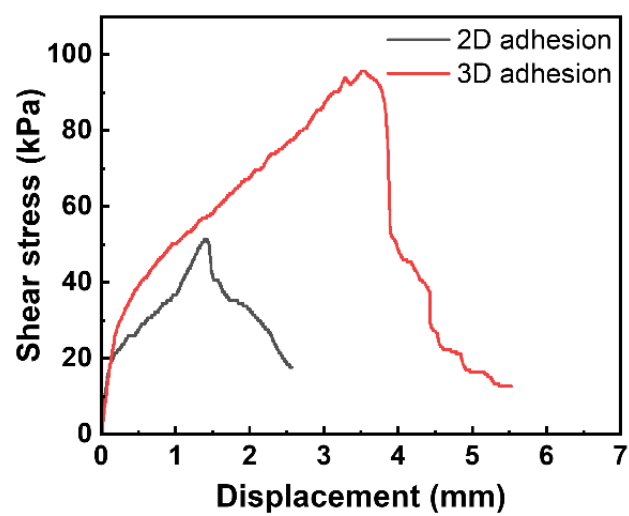


Figure S16. Stress–displacement curves obtained from lap shear tests of bioadhesive-treated INA-hydrogel with planar (2D) and pyramid (3D)-structured geometries.

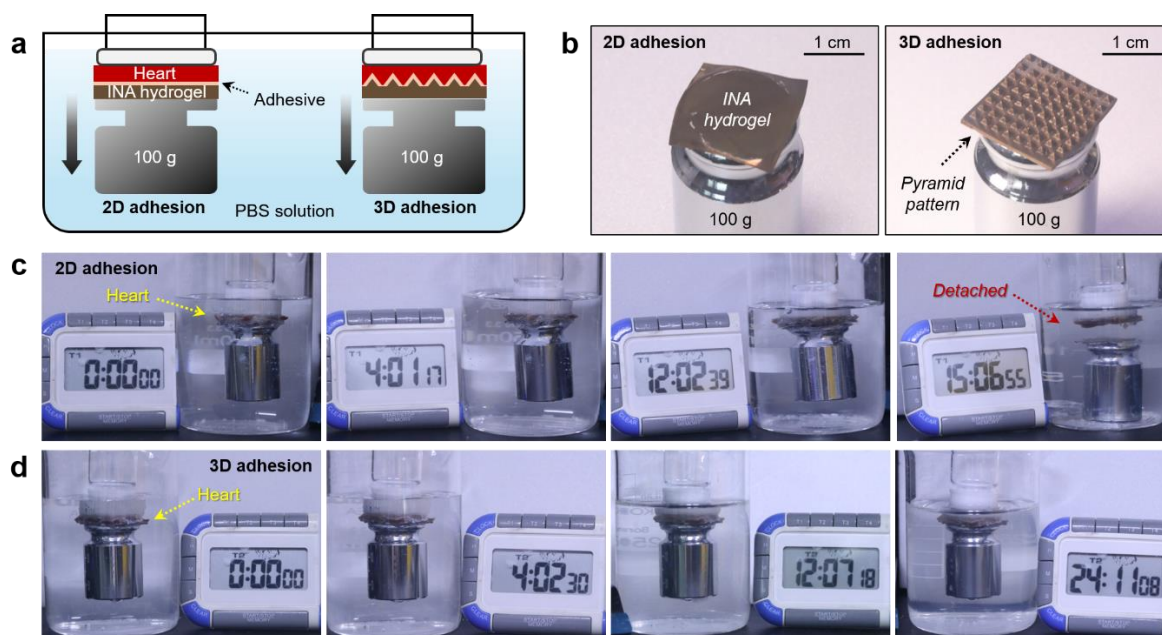


Figure S17. (a) Schematic illustration of long-term stability testing setup of bioadhesive-treated INA-hydrogel in PBS solution. (b) Photographic images of cyanoacrylate-based bioadhesive-treated INA-hydrogels with planar (2D) and pyramid (3D)-structured geometries before long-term immersion tests. (c-d) Photographic images of cyanoacrylate-based bioadhesive-treated INA-hydrogels with (c) planar (2D) and (d) pyramid (3D)-structured geometries during long-term immersion tests.

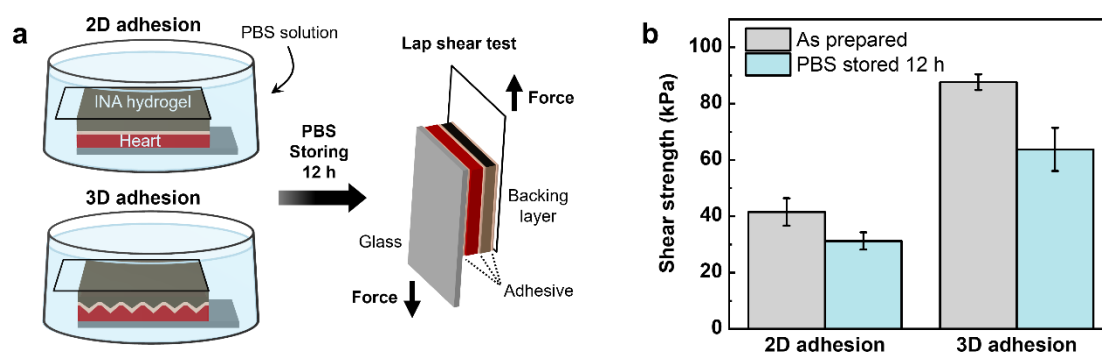


Figure S18. (a) Schematic illustration of bioadhesive-treated INA-hydrogels immersed in PBS solution. (b) Shear strength of cyanoacrylate-based bioadhesive-treated INA-hydrogel with planar (2D) and pyramid (3D)-structured geometries after dry state (air) and wet state (immersion in PBS solution for 12 h).

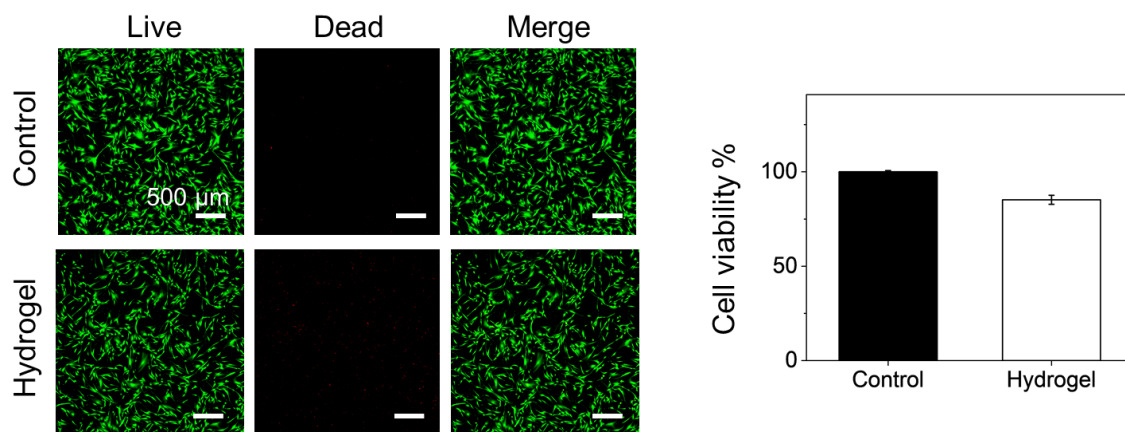


Figure S19. Representative Live/Dead fluorescence images and CCK-8 cell viability results of HDFs following extract treatment for 24 h. Live cells are shown in green and dead cells in red. Data are presented as mean $\pm$ SD. Scale bar = 500 μm .

Table S1. Comparative summary of previously reported hydrogel interfacial engineering techniques and our approach (interdigitated nanoparticle assembly).

Method	Material Compatibility	Process Feasibility	Property Retention	Adhesion Strength	Reference
Polymer rearrangement	<Substrate> - Limited hydrogel <Adherend> - Hydrophobic polymer	Interacting with hydrophobic mold	- nm-scale coating - Negligible effects in mechanical property	Weak (physical)	[27-28]
Polymer-brush grafting	<Substrate> - Limited hydrogel <Adherend> - None	- ATRP under Ar	- nm-scale coating - Negligible effects in mechanical property	None	[29-31]
Polymer anchoring	<Substrate> - Limited hydrogel <Adherend> - Hydrophobic polymer	Polymerization of hydrophobic monomers with initiator-absorbed hydrogel	- μ m-scale coating > 50% increase in Young's modulus	Strong (chemical)	[32-35]
NP physical adhesion	<Substrate> - Diverse hydrogel <Adherend> - Hydrogel - Polymer - Biological tissue	Applying the nanoparticle solution onto the hydrogel surface	- nm-scale coating - Negligible effects in mechanical property	Moderate (physical)	[38-42]
Our approach (INA)	<Substrate> - Diverse hydrogel <Adherend> - Small molecules - Polymer (PUA, PMMA, PET, PTFE, PFPE, rubber) - Glass, metal, mineral - Biological tissues	Immersing in TREN solution and TOA-AuNPs solution	- nm-scale coating - Negligible effects in mechanical property	Strong (chemical & physical)	