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Preferential Interfacial Engineering of Hydrogels via Interdigitated Nanoparticle Assembly

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ABSTRACT

Hydrogels have emerged as promising materials across various fields, including biomedical, electronic, and robotic applications, due to their intrinsic softness and biocompatibility. Despite these advantages, the development of hydrogel-based functional materials and devices remains limited by the narrow range of materials that can be seamlessly and robustly integrated with water-swollen hydrogel matrices. This interfacial incompatibility significantly restricts their functional expansion and practical applicability. Herein, we present a strategy for the facile integration of hydrogel with a broad spectrum of materials, including polymers, metals, and biological tissues, by employing interdigitated metal nanoparticle (NP) assembly to form nanobridges on hydrogel surfaces. This approach is based on ligand-exchange-assisted NP assembly, which induces strong affinity between metal NPs and the hydrogel matrix. The partially exposed NP domains act as nanobridges that mediate chemical or physical bonding with functional or even hydrophobic components. Notably, this approach enables effective use of commercial bonding agents onto hydrogel, regarded previously as incompatible with hydrogels, thereby extending their applicability as adhesives for biological tissues. This work establishes a broadly applicable platform for constructing a variety of hydrogel-based systems with versatile interfacial compatibility.

1 | Introduction

Hydrogels, characterized by a 3D soft polymeric network, retain substantial amounts of water, often exceeding 50% of the total volume. Their solid-like framework is generally formed through crosslinked hydrophilic polymers, while the aqueous phase permeates and swells the network. Owing to these unique chemical and structural features, hydrogels exhibit an unusual

combination of liquid- and solid-like characteristics that are rarely observed in other soft matter systems [1, 2]. Such attributes include tissue-like mechanical compliance, high biocompatibility, large deformability, chemical tunability, and responsiveness to diverse external stimuli. As a result, these properties have positioned hydrogels as promising materials for biomedical engineering [3–8], flexible electronics [7, 9, 10], soft robotics [11, 12], wearable/implantable devices [6, 7, 13, 14], environmental sensing

Hyeonjin Kim, Hyeseoung Lim, and Ji Min Lee contributed equally to this work.

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[14–16], and a variety of emerging technological applications [17, 18].

Despite this promise, several intrinsic constraints hinder their broader applicability [1, 2]. Conventional hydrogels are highly susceptible to dehydration in air, resulting in progressive degradation of mechanical integrity and functional performance over time. In addition, the integration of multifunctional components into hydrated polymer networks remains challenging, restricting the realization of advanced systems that require the simultaneous coupling of electrical, chemical, and mechanical functionalities. These critical drawbacks impede the application of hydrogels in robust, high-performance platforms for next-generation engineering and biological technologies.

To expand the utility of hydrogels, novel strategies are urgently needed to alleviate their intrinsic limitations and enable the incorporation of new functionalities without compromising their inherent material characteristics. Such strategies can be inspired by natural materials, where hydrogel-like biological matrices—such as fruits, fish eggs, and cartilage—have evolved structural and interfacial adaptations that preserve functionality under harsh environmental conditions. For example, fruits protect their hydrogel-like water-rich interiors through mechanically robust skins [19–21]; fish eggs employ multilayered membranes to withstand osmotic fluctuations [22]; and cartilage endures long-term mechanical loading through graded, integrated interfaces with adjacent bone and muscle [23]. Despite their diversity, these systems share a common design principle: the selective modification of surfaces or interfaces while maintaining the intrinsic properties of the internal hydrogel-like matrix. This principle provides a fundamental design strategy for engineering hydrogels that can maintain high functional integrity even under demanding environmental conditions.

Applying this natural design paradigm to synthetic hydrogels, however, remains highly challenging [24–26]. The abundance of internal water and the persistent hydration layer at the hydrogel surface impede stable interactions with externally introduced functional components. This hydrated interface weakens hydrogel polymer-outer component interactions and prevents the reliable adsorption of hydrophobic or mechanically dissimilar components, making preferential surface engineering particularly difficult. Consequently, achieving controlled interfacial assembly and stable integration of functional components at such water-rich and dynamic interfaces remains a significant scientific and technological challenge.

A variety of strategies have been explored to address these issues [27–36]. Previous approaches, including polymer surface rearrangement [27, 28], polymer-brush grafting [29–31], and polymeric coatings [32–35], have enabled meaningful progress in hydrogel surface modification (Table S1 and Figure S1). Specifically, polymer surface rearrangement utilizes hydrophobic interactions between the mold surface and the hydrogel polymer backbones during the polymerization process. These interactions drive the preferential migration of hydrophobic polymer chains toward the hydrogel surface, resulting in a surface enriched with hydrophobic segments. Consequently, nanoscale surface hydrophobicity is significantly enhanced while the bulk properties of the hydrogel remain essentially unaffected.

However, this strategy is applicable only to specific hydrogels and is generally incompatible with the integration of dissimilar materials. Polymer-brush grafting methods, which are typically based on surface-initiated atom transfer radical polymerization (ATRP), provide precise nanoscale control over surface features by growing polymer brushes directly from the hydrogel surface. Despite offering a high level of control, these approaches require complex processing steps and are confined to a limited range of hydrogels. They also struggle to achieve high brush density and thickness. Another strategy for introducing polymer layers onto hydrogel surfaces is polymer-anchoring-based coating, which relies on the adsorption of initiators onto the hydrogel surface followed by surface-confined polymerization in a monomer solution. Although the coating thickness can be controlled by adjusting the polymerization time, this approach has limited material versatility and may compromise the intrinsic properties of the hydrogel. Recently, a hydrogel surface modification method based on a hydrogel marble structure was introduced, enabling the formation of a uniform oil-polymer film on the hydrogel surface. Although this structure is easy to fabricate and is well suited for forming a mobile shell without significantly altering the mechanical properties of the hydrogel, the relatively weak adhesion between the constituent layers makes it difficult to achieve robust attachment to the hydrogel or construct a mechanically strong shell [37].

As an alternative to these traditional strategies, the concept of inorganic NP (mainly SiO_2)-mediated physical bridging has gained significant attention due to its conceptual simplicity and broad material compatibility [38–42]. In this approach, the NPs act as interfacial mediators that promote adhesion between hydrogels and external components. Specifically, once deposited onto the hydrogel surface, the NPs spontaneously assemble and become immobilized through physical adsorption. When an opposing polymeric substrate is brought into contact with the NP-coated hydrogel under applied pressure, the polymer chains from both interfaces adsorb onto the NP surface, thereby generating physical adhesion (Table S1). Although this method minimally perturbs the internal structure of hydrogels and is applicable to various hydrogel systems, its reliance on weak physical adsorption inherently limits the attainable adhesion strength, restricting both the precision and diversity of achievable surface functionalities. Moreover, its practical application has largely been restricted to the adhesion of polymeric and biological materials.

More broadly, these existing methods share inherent limitations: they may affect the bulk properties of the hydrogel, lack spatial specificity, exhibit poor compatibility with dissimilar materials, or fail to provide sufficiently strong and durable interfacial bonding. To the best of our knowledge, no current technique simultaneously satisfies the essential requirements of minimal impact on the hydrogel interior, controllable surface modification, broad material compatibility, and robust interfacial adhesion. The need for advanced interfacial engineering strategies is highlighted, capable of enabling stronger, more controllable, and more versatile functional integration at hydrogel surfaces.

In this work, we introduce an interfacial engineering strategy that overcomes the limitations of existing approaches for hydrogel surface modification. This strategy employs

interdigitated nanoparticle assembly (INA) as a robust and versatile nanobridging platform. Here, INA refers to a partially embedded and mechanically interlocked nanoparticle architecture formed at the hydrogel surface, in which nanoparticle assemblies are anchored within the interfacial region while remaining partially exposed for subsequent functionalization. Unlike conventional NP-mediated physical adhesion methods that rely on weak and reversible adsorption, the INA strategy is proposed to proceed through a ligand-exchange-assisted assembly of NPs directly at the hydrogel interface. Although direct evidence of ligand-exchange is not available in the present study, the proposed mechanism is supported by the selective accumulation of NPs at the hydrogel surface, spontaneous NP sintering, and the formation of interconnected NP assemblies, all of which are consistent with previous reports on amine-mediated ligand-exchange systems [43–47].

By simply loading multidentate amine molecules into hydrogels, this approach can be readily implemented without modifying the hydrogel synthesis, composition, or bulk network structure, thereby providing broad compatibility across diverse hydrogel systems. Specifically, the approach involves interfacial ligand-exchange between amine-containing small molecules incorporated within the hydrogel network and ligand-stabilized NPs dispersed in an immiscible phase [44, 45, 47]. In this process, the loaded amines serve both as active participants in the ligand-exchange with the NPs and as anchors between NPs and hydrogel by hydrogen bonding with hydroxyl groups in the hydrogel matrix. Based on these observations and previous studies of analogous amine-mediated NP assembly systems, this ligand-exchange reaction is proposed to promote the selective accumulation of NPs at the hydrogel interface, followed by NP sintering and assembly into interlocked nanoparticle clusters on the hydrogel surface. Therefore, we referred to “interdigitated” to describe this mutually interconnected morphology of nanoparticle assemblies, in which parts of the assemblies are embedded into the hydrogel surface while remaining partially exposed above the interface. Consequently, these NP assemblies are expected to function as mechanically robust and chemically addressable interfacial nanobridges, whose density, coverage, and spatial distribution can be precisely modulated without perturbing the bulk properties of the hydrogel.

The exposed surfaces of the interdigitately assembled NPs provide a highly adaptable interfacial platform capable of mediating chemical or physical interactions with a wide range of materials that are typically difficult to integrate with hydrogels due to poor interfacial affinity. Notably, INA enables robust adhesion to diverse classes of materials, including small-molecule linkers, hydrophobic or fluoropolymers, which can be utilized to modify the NP surface chemistry through post-assembly surface functionalization, thereby effectively decoupling the hydrogel network chemistry from the interfacial functionality. This strategy substantially expands the usability of commercial bonding agents that are conventionally incompatible with hydrogels, particularly hydrophobic adhesives such as cyanoacrylate-, epoxy-, and polyurethane-based systems, which typically fail on water-rich, slippery hydrogel surfaces. By transforming the hydrogel interface into a mechanically stable and hydrophobic NP-mediated layer, the INA enables these adhesives to function

effectively even on hydrated substrates and delicate biological tissues. As a result, whereas conventional tissue adhesives typically exhibit adhesion strengths of 5–15 kPa, the INA-hydrogels achieved adhesion strength exceeding 70 kPa, demonstrating a significantly enhanced adhesive performance even for otherwise non-adhesive conventional hydrogels. Based on this capability, we further demonstrate that the INA-mediated adhesion enables reliable wound sealing and fluid-tight closure of perforated tissues, suggesting its potential utility in biomedical and surgical applications.

Overall, the INA strategy represents a simple, flexible, and substrate-independent approach to hydrogel interfacial engineering, enabling selective and controllable surface modification while largely preserving the intrinsic properties of the hydrogel interior. Importantly, this approach simultaneously achieves broad material compatibility and strong interfacial adhesion—an outcome that remains challenging for conventional coating strategies. Taken together, we believe that our approach based on INA can provide a basis for developing multifunctional hydrogel materials and devices.

2 | Results and Discussion

2.1 | Interdigitated NP Assembly on Hydrogels

To induce the interdigitated NP assembly on hydrogel surfaces, we employed a two-step sequential immersion process (Figure 1a). First, a commonly used acrylic acid-acrylamide copolymer hydrogel was selectively synthesized and employed as a model system. The as-prepared hydrogel was immersed in an aqueous solution of amine (NH_2)-functionalized tris(2-aminoethyl)amine (TREN, $M_w \sim 146$), allowing TREN molecules to diffuse into the carboxylic acid (COOH)-functionalized hydrogel matrix through hydrogen-bonding interaction between the COOH of the hydrogel and NH_2 groups of TREN. The TREN-incorporated hydrogel was then immersed in a toluene dispersion of tetraoctylammonium-stabilized AuNPs (TOA-AuNPs).

At this stage, the TREN-rich aqueous phase present at the hydrogel surface and a nonpolar AuNPs (diameter ~ 7 nm) dispersion in toluene spontaneously formed a biphasic interfacial region (Figure 1b). Although direct molecular-level evidence for ligand exchange was not obtained in the present study, the observed nanoparticle assembly behavior, together with previous reports on analogous amine-mediated systems, suggests that ligand exchange is the most plausible mechanism governing the interfacial assembly process. Within this interfacial region, multidentate NH_2 groups of TREN were considered to interact with the AuNP surface and replace the bulky TOA ligands at the hydrogel interface. This process enables the robust assembly of AuNPs on the hydrogel surface through strong coordination interactions with the amine groups of the TREN-incorporated hydrogel, while partial penetration into the network further stabilizes their anchoring. Importantly, the proposed amine-mediated assembly is not unique to TREN. Other amine-containing chemicals, including diethylenetriamine (DETA) and poly(ethyleneimine) (PEI), also promote the assembly of AuNPs on hydrogel surfaces through analogous reactions, indicating that the presence of amine groups is the key point for the INA

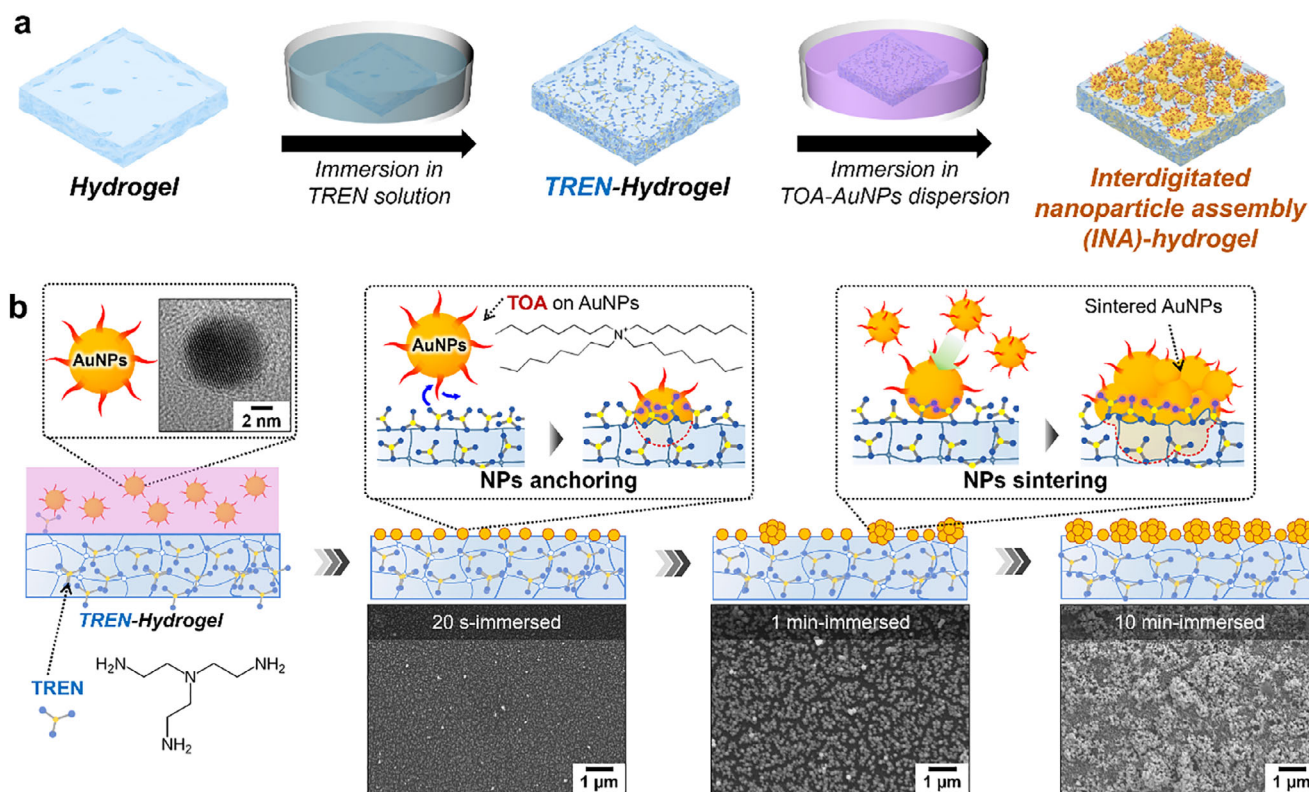


FIGURE 1 | (a) Schematic illustration of the overall process for inducing interdigitated nanoparticle assembly on hydrogels via a two-step sequential solution immersion. (b) Detailed schematic illustration of the interfacial phenomena occurring at the hydrogel-TOA-AuNP solution interface when TREN-incorporated hydrogels are immersed in a TOA-AuNP solution. High-resolution transmission electron microscopy (TEM) images of the TOA-AuNPs and top-view scanning electron microscopy (SEM) images obtained at different immersion times (20 s, 1 min, and 10 min) are included to clearly illustrate the time-dependent nanoparticle assembly and surface evolution.

process (Figure S2). In particular, during this amine-mediated NP assembly, adjacent AuNPs underwent spontaneous sintering accompanied by particle size growth, even under ambient temperature and pressure. Although the molecular process leading to NP fusion was not directly monitored, the observed sintering behavior is consistent with a proposed ligand-exchange-mediated reduction in interparticle spacing. For AuNPs with relatively low cohesive energy, when the interparticle distance is reduced below approximately 5–7 Å [43–47], the strong metallic bonding induced by metal atomic diffusion can be formed between neighboring AuNPs. In contrast, the hydrogels without TREN incorporation did not exhibit the adsorption of TOA-AuNPs, implying negligible affinity between bare hydrogel and TOA-AuNPs. Negatively charged AuNPs dispersed in aqueous media can also be assembled onto the TREN-incorporated hydrogel surface through electrostatic interaction. However, the electrostatic repulsion occurring among the same charged AuNPs prevents the formation of densely packed NP arrays, resulting instead in a sparsely adsorbed AuNP layer without inducing NP sintering [48].

Previous computational studies further support this mechanism. In the previous density functional theory (DFT) study [44], small amine-containing linkers such as DETA and TREN were shown to adopt flattened conformations on Au surfaces, forming a nearly atomic-scale organic layer between adjacent Au surfaces with an optimal separation distance of approximately 7 Å. This reduced

interparticle spacing was suggested to promote metallic fusion between neighboring AuNPs during amine-mediated assembly. In addition, atomistic molecular dynamics (MD) simulations of TREN confined between adjacent Au surfaces showed that, when the Au surfaces were covered by a TREN monolayer adopting a flat conformation, the minimum separation distance was reduced to approximately 5.6–5.7 Å. Such a minimized interparticle distance between AuNPs with relatively low cohesive energy can facilitate reciprocal atom diffusion, thereby promoting partial metallic fusion and the formation of interconnected AuNP assemblies [43, 46]. Although these computational results were obtained for analogous systems rather than the present experimental configuration, they are in good agreement with the spontaneous NP sintering and interconnected NP assemblies observed experimentally in this work, providing indirect support for the proposed ligand-exchange-mediated INA mechanism.

To further examine the spatial distribution of AuNP adsorption within the hydrogel, energy-dispersive X-ray spectroscopy (EDS) mapping was performed on the interdigitated NP-assembled hydrogel (hereafter referred to as INA-hydrogel) using cryo-field emission-scanning electron microscopy (cryo-FE-SEM) (Figure 2a). The cross-sectional analysis demonstrated that Au signals were predominantly localized near the surface and appeared partially embedded within the hydrogel interior. These observations indicate that the NP assemblies primarily occurred at the interface between the hydrophilic hydrogel surface and

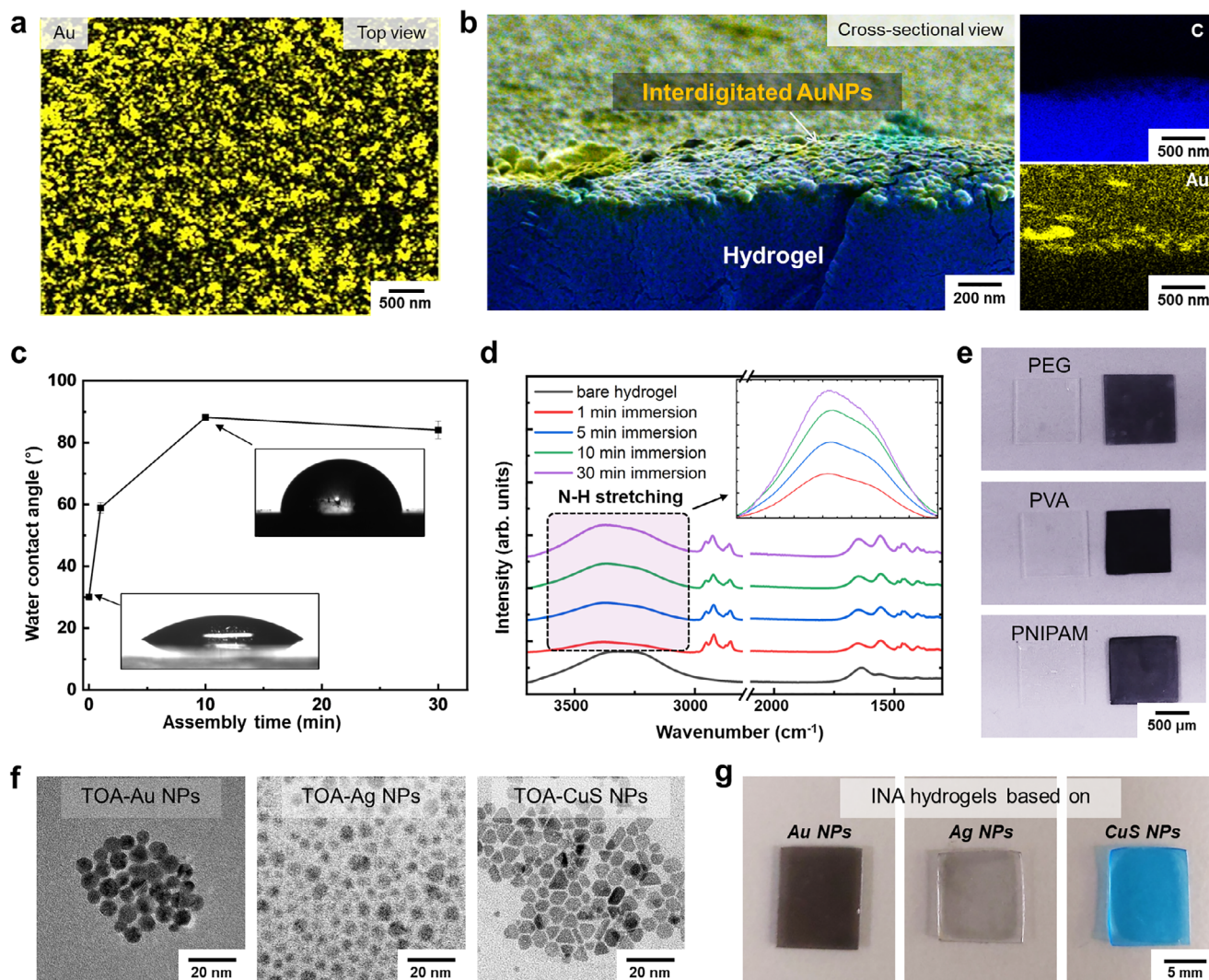


FIGURE 2 | Energy-dispersive X-ray spectroscopy (EDS) analysis of 10 min immersed INA-hydrogels showing (a) top view Au elemental view and (b) cross-sectional elemental maps showing (left) the combined elemental distribution and (right) the individual distributions of C (top) and Au (bottom), confirming the uniform incorporation and distribution of AuNPs throughout the hydrogel network. (c) Changes of water contact angles measured on INA-hydrogels as a function of immersion time. (d) Fourier transform infrared (FT-IR) spectra of bare and INA-hydrogels (1–30 min); inset: enlarged 3000–3800 cm⁻¹ region. (e) Photographs of bare and INA-coated PEG, PVA, and PNIPAM hydrogels. (f) TEM images of TOA-stabilized Au, Ag, and CuS nanoparticles. (g) Photographs of INA-hydrogels assembled with different nanoparticles.

hydrophobic TOA-AuNPs solution. Although the molecular-level assembly mechanism was not directly verified, the selective localization of AuNPs at the surface is consistent with the proposed ligand-exchange reaction.

For further elucidate this phenomenon, we systematically investigated the assembly behavior of TOA-AuNPs as a function of NP assembly time (Figure 2b; Figures S3 and S4). During the initial 10 min, the AuNPs rapidly anchored to the hydrogel surface, effectively covering the majority of the area within the first 20 s. This was subsequently followed by the formation of larger NP assemblies (diameter: 178 ± 12 nm) and an NP layer (thickness: 216 ± 14 nm) through interparticle sintering (Figures 2b and S3). Cross-sectional high-resolution transmission electron microscopy (HR-TEM) and focused ion beam scanning electron microscope (FIB-SEM) imaging revealed that the nanoparticle assemblies were partially embedded within the hydrogel surface

rather than merely deposited on top of it (Figure S3). This partially embedded architecture is expected to mechanically anchor the coating layer to the substrate, providing structural evidence supporting the proposed interdigitated nanoparticle-hydrogel interface. After 30 min, the NP assemblies exhibited lateral interconnectivity, evolving into thin plate-like structures that were susceptible to cracking in response to hydrogel volume changes (Figure S4). This time-dependent morphological transformation was further supported by water contact angle measurements (Figure 2c). The contact angle, determined in relation to assembly time, peaked at approximately 89° after 10 min. Notably, the morphology formed at 10 min significantly increased the effective surface area, thereby facilitating more efficient surface modification of the hydrogel.

To obtain further indirect evidence for the proposed ligand-exchange-mediated NP assembly behavior, Fourier-transform

infrared (FTIR) spectroscopy was performed as a function of NP assembly time (Figure 2d), based on the characteristic vibrational features of TREN and TOA-AuNPs. The pristine TREN spectrum displays the N–H stretching bands in the 3300–3400 cm^{-1} region (Figure S5a), whereas pristine TOA-AuNPs exhibit the C–H stretching bands at 2850 and 2920 cm^{-1} , arising from the long alkyl chains of bulky TOA ligands (Figure S5b). Upon assembly of TOA-AuNPs onto the hydrogel matrix, the emergence and gradual intensification of the C–H stretching bands were clearly observed, confirming the successful immobilization of TOA-AuNPs on the hydrogel surface (Figure S5c). Notably, the N–H stretching bands progressively increased with increasing assembly time, indicating a systematic evolution of the chemical environment of amine groups during the assembly process. This behavior suggests a time-dependent increase in surface coverage of AuNPs accompanied by ligand-exchange processes at the AuNP-hydrogel interface. The concurrent enhancement of the N–H-related bands further imply that, beyond simple physical adsorption, specific chemical interactions are involved in the assembly process. To further examine the evolution of the ligand behavior, we additionally analyzed layer-by-layer (LbL)-assembled multilayers $(\text{TREN/TOA-AuNP})_n$ (Figure S5d). The TOA rich surfaces ($n = 1$ and 2) exhibited relatively stronger C–H stretching signals than the TREN treated surfaces ($n = 1.5$ and 2.5), indicating a substantial change in the relative contribution of TOA- and TREN-associated species at the AuNP surface. Although, these FTIR results alone cannot directly distinguish ligand-exchange at the molecular level, the observed changes are consistent with partial exchange of TOA ligands by TREN during the assembly process.

Further indirect evidence was obtained from X-ray photoelectron spectroscopy (XPS) analysis (Figure S6). The Br3d spectrum of the pristine TOA-AuNPs exhibited a peak at binding energy of 67.0 eV originating in TOABr ligands, whereas the peak was no longer detected after TREN treatment. The disappearance of the Br3d signal is consistent with the removal or substantial reduction of TOA ligands, providing additional indirect support for the proposed ligand-exchange. Nevertheless, because XPS cannot directly distinguish the Au–N coordination associated with TOA and TREN, this result alone does not constitute direct confirmation of ligand-exchange. Taken together, although FTIR and XPS results cannot directly provides molecular level confirmation of ligand-exchange, the observed spectral evolution, together with the selective interfacial assembly of AuNPs, spontaneous NP fusion, and previous DFT/MD studies on analogous amine-mediated systems, consistently supports the proposed ligand-exchange reaction between bulky TOA ligands bound to the AuNP surface and amine functionalities of TREN-incorporated hydrogel, along with electrostatic and hydrogen-bonding interactions between TREN and the hydrogel network. Therefore, ligand-exchange is considered the most plausible explanation for the formation of INA strategy which produced the robust adhesion of AuNPs onto the hydrogel.

This strategy is readily applicable to a diverse array of hydrogel systems, including polyethylene glycol (PEG), poly(vinyl alcohol) (PVA), and poly(N-isopropylacrylamide) (PNIPAM), all of which readily accommodate TREN incorporation and subsequent AuNP

assembly using identical experimental procedures (Figure 2e). The consistent formation of interdigitated AuNP layers across these chemically distinct hydrogels suggests that the assembly process is governed by general physicochemical characteristics of hydrogels, rather than by specific polymer chemistries. Furthermore, successful extension of this approach to other NP systems, including TOA-stabilized Ag and CuS NPs (Figure 2f,g), further emphasizes the versatility of the ligand-exchange-driven assembly process and its broad compatibility with diverse metallic and semiconducting NP compositions.

These INA-hydrogels revealed significant advantages over conventional surface modification methods. The strong embedding of AuNPs within the hydrogel matrix was confirmed by a tape-peeling test (Figure 3a). In this test, an adhesive tape was repeatedly applied and removed, and the resulting changes were evaluated through visual inspection and water contact angle measurements (Figure 3b). Notably, no noticeable change was observed in the photographic images of the hydrogel surface. Although a slight decrease in the water contact angle was observed up to approximately 30 peeling cycles, this angle remained stable thereafter, implying that the AuNP-assembled surface exhibited enduring stability. This possibility was further confirmed by SEM analysis. As shown in Figure 3c, the surface morphology observed after 50 peeling cycles revealed that the repeated application of adhesive tape removed only a weakly bound outer layer, while the underlying interfacial NP layer remained intact. These results indicate that the AuNP layer is strongly integrated with the hydrogel matrix, making the removal of the assembled NPs difficult without inducing cohesive failure of the hydrogel itself. Importantly, despite the formation of a mechanically robust NP layer at the hydrogel surface, the INA treatment did not substantially alter the intrinsic mechanical properties of the hydrogel bulk. The mechanical properties of pristine and INA-treated hydrogels were therefore compared by tensile measurements (Figure S7). No significant differences in Young's modulus were observed before and after INA treatment, indicating that the nanoparticle assembly was predominantly confined to the near-surface region without appreciably perturbing the bulk hydrogel network. These results further support the surface-selective nature of the INA strategy, which enables robust interfacial modification while preserving the intrinsic mechanical properties of the underlying hydrogel.

Interestingly, we found that a distinctive feature of these INA-hydrogels is their high permeability despite the presence of dense NP coating (Figure 3d). When a dye solution (i.e., Rhodamine B dissolved in DI water) was applied, the dye molecules readily diffused through the AuNP layer into the hydrogel interior (Figure 3e). This behavior represents a significant advantage over conventional surface modification strategies [29–33], which often involve relatively thick interfacial layers that hinder molecular permeation. Moreover, conventional modification methods typically rely on planar processing conditions or involve complicated procedures, making it difficult to achieve uniform coverage on substrates with 3D geometries (Figure 3f) [27–33, 38–42]. Collectively, these findings highlight the structural adaptability and broad applicability of the INA strategy across substrates with diverse surface topographies.

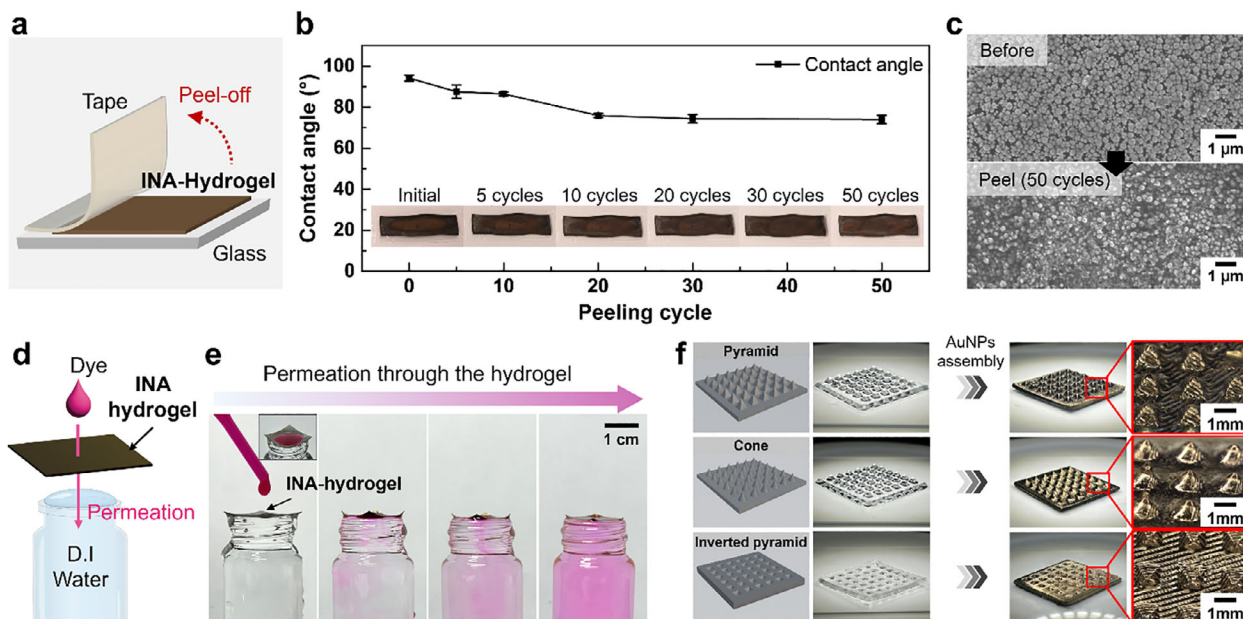


FIGURE 3 | (a) Schematic illustration of the tape-peeling test performed on INA-hydrogels. (b) Water contact angle changes as a function of peeling cycle number. (c) SEM images of the INA-hydrogel surface before and after repeated peeling (50 cycles). (d) Schematic illustration of the dye permeation test for INA-hydrogels. (e) Photographic images showing dye permeation through the INA-hydrogel and subsequent diffusion into deionized (DI) water. (f) Photographic images of pyramid-, cone-, and inverted pyramid-structured hydrogels before and after INA-coating on hydrogels, along with enlarged optical images of the surface structures.

2.2 | Surface Modification of INA-Hydrogels With Small Molecules

With well-defined NP assemblies established on various hydrogels, we next sought to further tailor the surface properties of the INA-hydrogels through additional surface functionalization processes. The residual native TOA ligands and newly adsorbed TREN molecules present on the surfaces of AuNPs within the INA-hydrogels can be readily displaced by simply immersing the samples in precursor solutions containing thiol (SH)-terminated small molecule linkers. Owing to the strong affinity of $-SH$ groups toward Au surfaces, arising from the formation of stable $Au-S$ bonds, this thiol-mediated surface modification proceeds efficiently under mild conditions (Figure 4a) [49, 50].

The effectiveness of this additional ligand exchange on INA-hydrogels was verified by FT-IR spectroscopy before and after the exchange process (Figures 4b and S8). Upon exchange with 1-dodecanethiol (abbreviated as C12-SH) or 1-octadecanethiol (C18-SH), a characteristic thiol-derived peak at 717 cm^{-1} appeared, which was absent in the pristine INA-hydrogels [51]. In addition, ligand-specific vibrational features were observed after exchange with other thiolated molecules, including a peak at 1045 cm^{-1} corresponding to the hydroxyl vibration of 2-mercaptoethanol (denoted as OH-SH) [52] and peaks at 1143 and 1199 cm^{-1} attributable to the C-F stretching modes of 1H,1H,2H,2H-perfluorodecanethiol (denoted as F-SH) [53]. Although FTIR alone cannot directly verify ligand replacement at the molecular level, the change of ligand-specific vibrational features strongly supported that the surface chemistry of INA-hydrogels can be effectively tuned using a diverse set of thiol-terminated linkers.

The corresponding changes in surface wettability were quantitatively evaluated by static water contact angle measurements (Figure S9). The original INA-hydrogels exhibited a moderately hydrophobic surface with a contact angle of approximately $\sim 89^\circ$. Following thiol-mediated surface modification with C12-SH ($\sim 102^\circ$), C18-SH ($\sim 117^\circ$), and F-SH ($\sim 120^\circ$), the surface hydrophobicity increased progressively, consistent with the decreasing surface energies of these ligands. In contrast, the INA-hydrogels modified with OH-SH displayed a substantially reduced contact angle of $\sim 68^\circ$, reflecting the hydrophilic nature of OH groups. These results supported that the surface wettability of INA-hydrogels can be precisely and predictably regulated through proposed thiol-mediated ligand-exchange.

Furthermore, spatially selective surface modification was achieved through localized treatment using SH-loaded filter papers (Figure 4c). Filter papers impregnated with hydrophilic OH-SH and hydrophobic F-SH were placed onto designated regions of the INA-hydrogel for 10 min, resulting in well-defined wettability patterns. Specifically, the OH-SH-treated region (left side) exhibited a hydrophilic surface with a contact angle of $\sim 68^\circ$, whereas the F-SH-treated region (right side) showed a markedly hydrophobic surface with a contact angle of $\sim 120^\circ$ (Figure 4d). These results demonstrate that selective surface functionalization and patterning can be readily achieved, enabling localized and programmable control over hydrogel surface properties.

2.3 | Stable Hydrophobic Polymer Coating on INA-Hydrogels

Another notable advantage of our approach is that hydrophobic surface modification of INA-hydrogels using small molecule

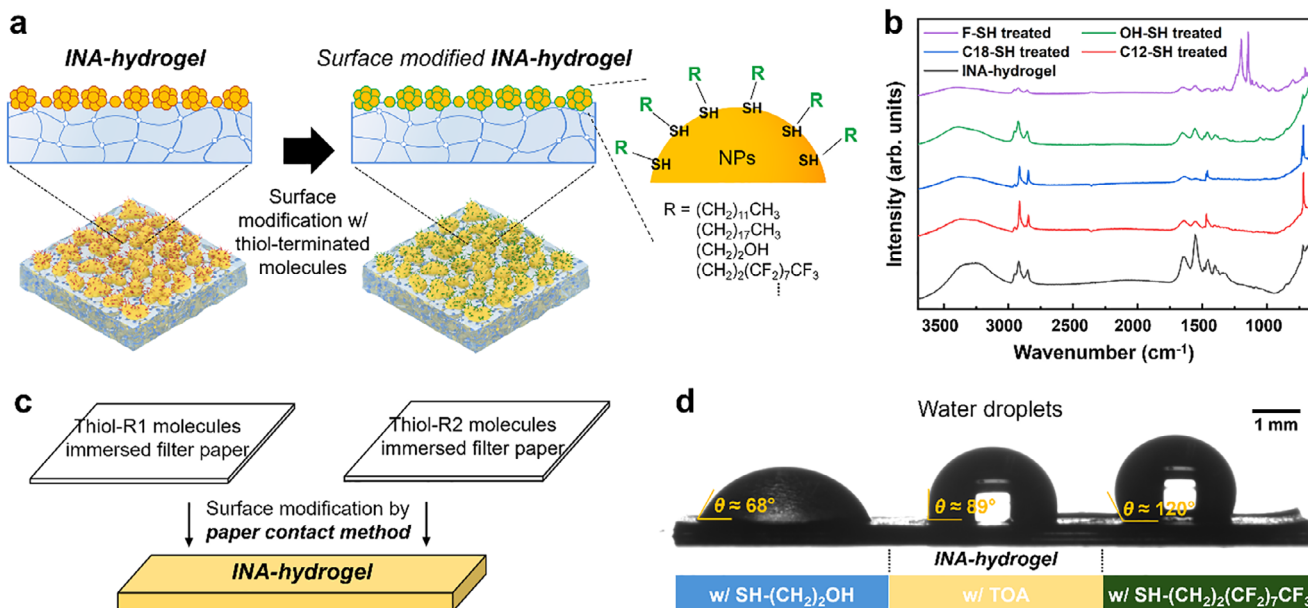


FIGURE 4 | (a) Schematic illustration of interfacial engineering of INA-hydrogels with various small molecules by self-assembled monolayers on exposed NPs-assembly surfaces. (b) FT-IR spectra of INA-hydrogel (immersion time: 10 min) after treating different small molecule linkers. (c) Schematic illustration of spatial patterning of INA-hydrogels with different surface modifications using a paper contact method. (d) Photographic image of INA-hydrogel (immersion time: 10 min) treated with different small molecule linkers on different positions showing capability of patterning by our approach.

linkers enables the formation of stable hydrophobic polymer coatings on hydrogel surfaces, thereby effectively overcoming the intrinsic hydrophilicity of hydrogels. To demonstrate this capability, we show that a variety of hydrophobic polymers—including poly(tetrafluoroethylene) (PTFE), poly(methyl methacrylate) (PMMA), UV-crosslinked poly(urethane acrylate) (PUA), UV-crosslinked polysiloxane (PSO), and perfluoropolyether (PFPE)—can be uniformly coated onto the INA-hydrogel surfaces (Figure 5a).

We first investigated the formation of a stable PUA coating layer on AuNP-assembled hydrogels. As shown in Figure 5b,c, the cross-sectional FE-SEM and optical microscopy (OM) images exhibited the formation of a well-defined PUA coating layer across the entire INA-hydrogel surface, indicating that the assembled AuNPs act as interfacial nanobridges between the hydrogel substrate and the polymer coating. In particular, the PUA layer remained firmly attached even under both inward and outward bending conditions (Figure 5c). Moreover, the thickness of the cross-linkable polymer coating layer could be effectively tuned through repeated deposition cycles and UV crosslinking. An initial PUA layer with a thickness of approximately 155 μm was formed on the INA-hydrogel, as confirmed by the cross-sectional OM imaging (Figure S10). Subsequent coating and UV crosslinking cycles resulted in a gradual and controllable increase in the overall coating thickness. This strategy was also applicable to various crosslinkable polymer systems, verified by cross-sectional OM images (Figure 5d).

These robust polymer coatings markedly enhanced the anti-dehydration performance of the hydrogels by suppressing the water evaporation through the hydrophobic barrier (Figure 5e). To quantitatively evaluate this effect, the weight retention of

bare and polymer-coated INA-hydrogels was monitored over a period of 7 days (Figures 5f,g, and S11). While the uncoated hydrogel rapidly dehydrated within a few hours, the hydrogels coated with UV-crosslinked PUA or PSO retained more than 80% of their initial weight after 7 days. Notably, the anti-dehydration performance was further improved by incorporating a nonvolatile silicone oil into the polymer layer. Following a previously reported method [32], the polymer-coated hydrogels were immersed in hot silicone oil (120°C) for 15 min and subsequently quenched in cold silicone oil (25°C) for 15 min. The resulting oil-infused polymer coatings exhibited exceptional anti-dehydration behavior, maintaining up to 96% of their initial weight. Taken together, these results demonstrate that robust hydrophobic polymer coatings enabled by INA significantly enhance the long-term structural and functional stability of hydrogels.

2.4 | Strong Adhesion of INA-Hydrogels onto Engineering Solids and Biological Tissues

Given their broad material compatibility and tunable surface properties, the INA-hydrogels exhibit significantly enhanced interfacial interactions with external materials, enabling strong adhesion to diverse substrates when combined with hydrophobic commercial adhesives. This behavior is particularly noteworthy because conventional adhesives typically perform poorly in water-rich environments, owing to their susceptibility to moisture and weak interactions with hydrated hydrogel networks (Figure 6a). In contrast, the hydrophobic interface introduced by the NP assemblies effectively overcomes these limitations by providing a compatible surface that enables hydrophobic commercial adhesives to function reliably even on wet and slippery hydrogel substrates (Figure 6b).

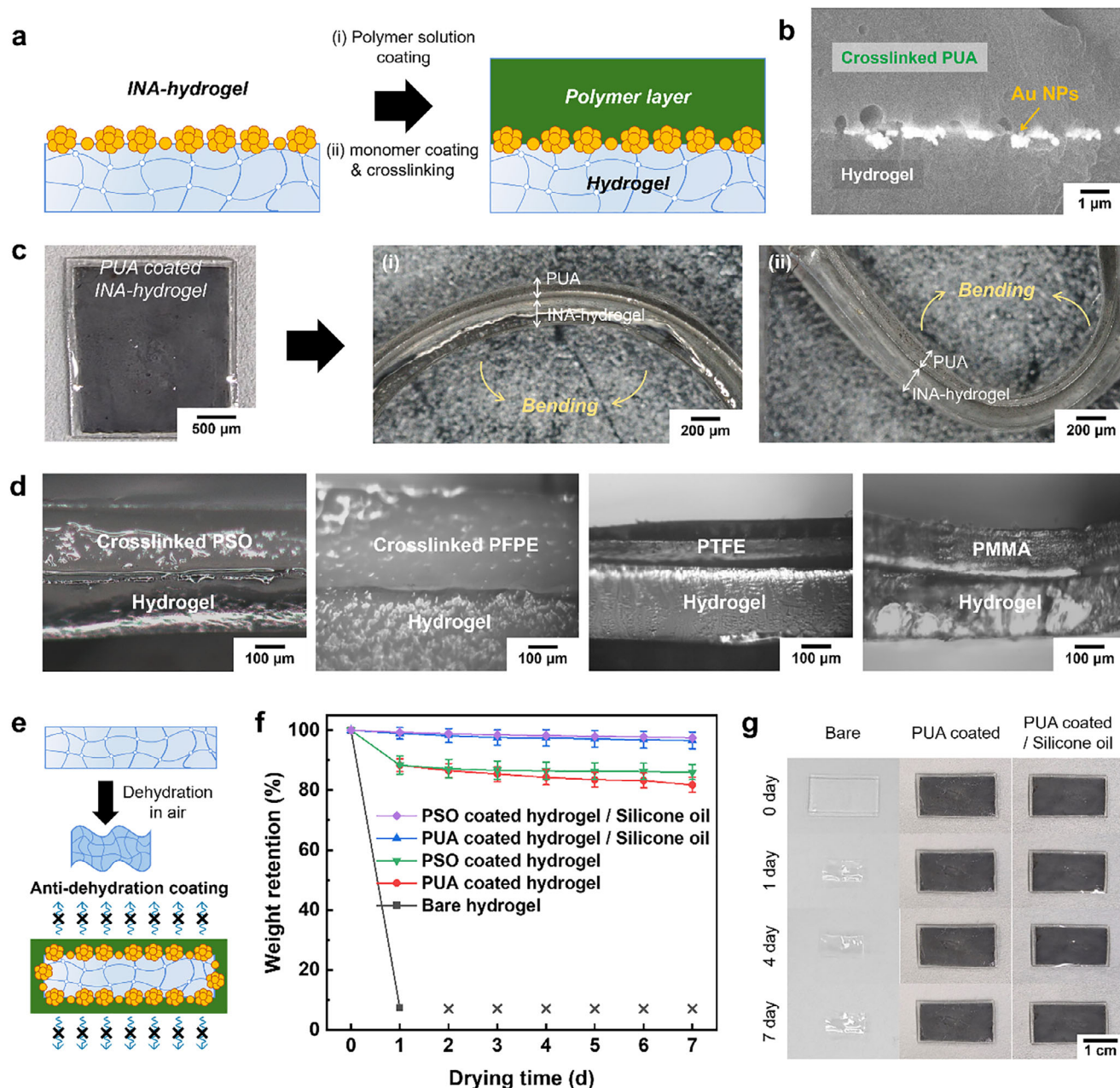


FIGURE 5 | (a) Schematic illustration of deposition of polymeric layer on INA-hydrogels bridged by interdigitated NPs assembly. (b) Cross-sectional SEM image of PUA deposited on INA-hydrogel. (c) Photographic images of PUA-deposited INA-hydrogel and cross-sectional OM images under (i) outward bending and (ii) inward bending conditions, demonstrating robust interfacial stability. (d) Cross-sectional OM images of various polymeric layers (PSO, PFPE, PTFE, and PMMA) deposited on INA-hydrogel surfaces. (e) Schematic illustration of anti-dehydration coating achieved by polymer layer formation on INA-hydrogels. (f) Weight retention of polymer deposited INA-hydrogels and silicone oil immersed polymer deposited INA-hydrogels for 7 days. (g) Photographic images of bare, PUA deposited, silicone oil infused PUA deposited INA-hydrogels for 7 days.

Adhesion performance was evaluated using lap shear with representative commercial adhesives, including cyanoacrylate-, epoxy-, and polyurethane-based adhesives (Figure 6c). When a widely used cyanoacrylate-based instant adhesive was applied to pristine hydrogels and bonded to glass, a low adhesion strength of ~15 kPa was observed (Figure 6d) primarily due to interfacial slippage caused by the highly hydrated surface (Figure 6e). In contrast, application of the same adhesive to INA-hydrogels resulted in a markedly enhanced adhesion strength exceeding 70 kPa. Under these conditions, cohesive failure of the hydrogel substrate occurred, preventing direct measurement of the inter-

facial adhesion limit. To enable more accurate quantification, the hydrogels were partially dried for 1 h to increase their mechanical stiffness prior to testing. Under these conditions, interfacial adhesion failure was observed, and the measured adhesion strength reached approximately 140 kPa.

Similar trends were observed for epoxy- and polyurethane (PU)-based adhesives (Figure 6f). On pristine hydrogels, both adhesives showed low adhesion strengths of 5.7 kPa using epoxy-based adhesive and 13.8 kPa using PU-based adhesive due to slippage at the hydrated interface. On the other hand, the

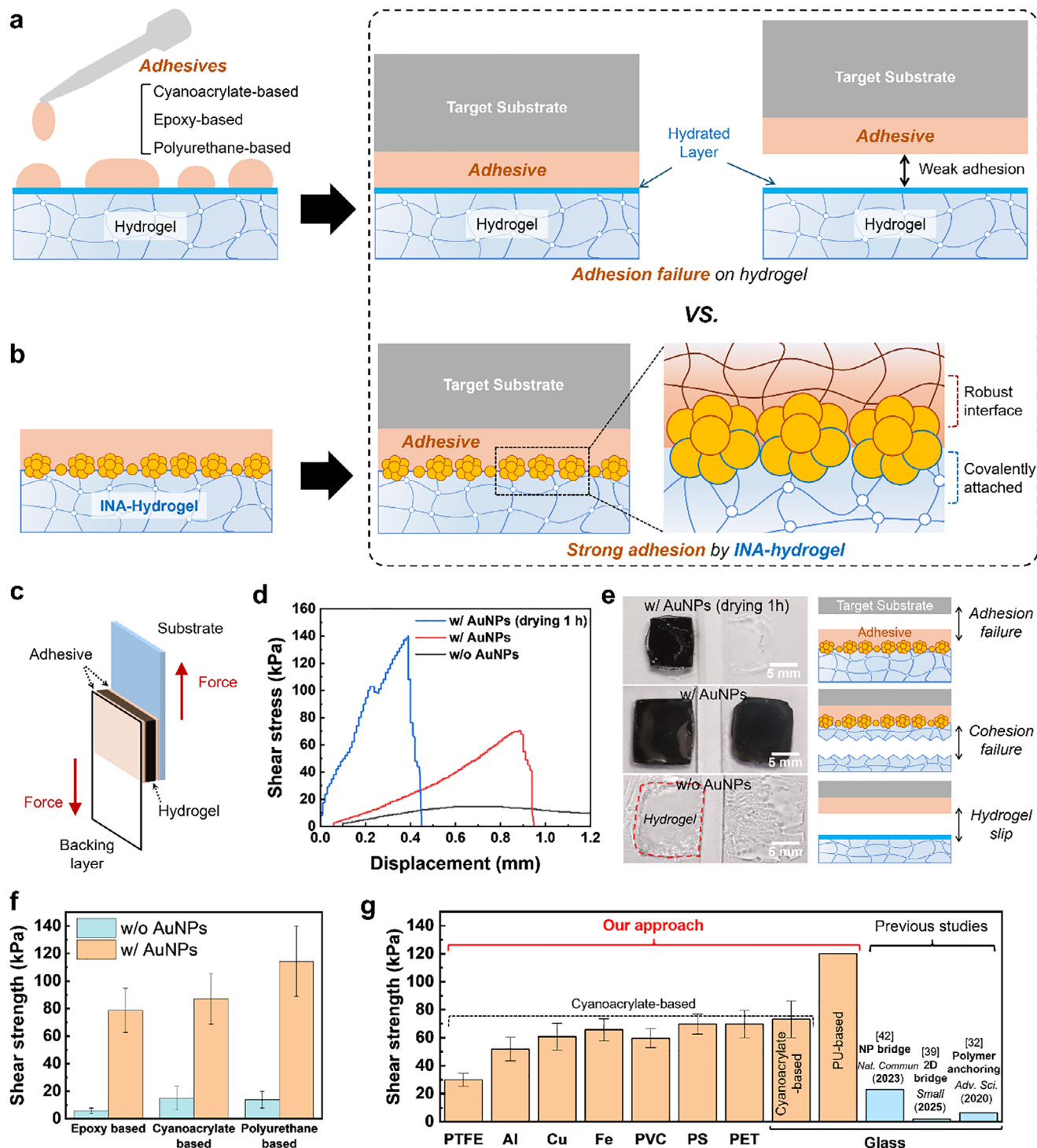


FIGURE 6 | Schematic illustration of adhesives applied (a) on bare hydrogels showing weak adhesion due to the hydrated interfacial layers and (b) on INA-hydrogels showing enhanced interfacial adhesion enabled by nanoparticle assembly-mediated nanobridging. (c) Schematic illustration of the lap shear test to evaluate the adhesion strength of adhesive-treated INA-hydrogels. (d) Stress-displacement curves obtained from lap shear tests of bare hydrogels, INA-hydrogels, and partially dried INA-hydrogels treated with a cyanoacrylate-based adhesive. (e) Photographic images and corresponding schematics after lap shear testing, illustrating interfacial adhesion failure, cohesive failure, and hydrogel slippage. (f) Adhesion shear strengths of INA-hydrogels measured using different commercial adhesives, including epoxy-, cyanoacrylate-, and polyurethane-based systems. (g) Summary of adhesion performance of the INA strategy across various substrates, along with comparison to previously reported hydrogel surface modification methods.

INA-hydrogels exhibited substantially higher adhesion strengths exceeding ~ 110 kPa, indicating significantly improved interfacial bonding with the aid of the INA layer on the hydrogel. Moreover, the INA-hydrogels maintained stable adhesion after 20 loading cycles without interfacial failure, indicating excellent resistance to repeated mechanical stress (Figure S12).

To investigate the origin of the enhanced adhesion, the wettability of INA-hydrogels was evaluated using representative hydrophobic liquids, including *n*-hexane, toluene, and silicone oil. Regardless of INA treatment time, all liquids exhibited contact angles below 10° and rapidly spread across the hydrogel surface, and the INA-hydrogels exhibited slightly lower contact angles than bare hydrogels, indicating favorable wetting of the INA-modified interface (Figure S13). However, despite the similarly low contact angles, lap-shear measurements revealed that adhesion strength increased progressively with INA treatment time and reached a plateau after 10 min (Figure S14). These results suggest that the nanoparticle-mediated surface morphology of INA plays a critical role in strengthening interfacial adhesion. Furthermore, the strong integration of the INA layer was obtained by examining the fracture surfaces after adhesion testing. At short INA treatment times, residual NP coatings were frequently observed on the adhesive side, indicating interfacial failure due to insufficient anchoring of the nanoparticle layer to the hydrogel substrate. In contrast, for samples treated for more than 10 min, the INA layer remained firmly attached to the hydrogel, and failure predominantly occurred within the hydrogel bulk. This transition from interfacial failure to cohesive failure indicates that the INA layer becomes strongly integrated with the hydrogel surface.

The adhesion capability of INA-hydrogels was further evaluated across a variety of engineering substrates beyond glass. As shown in Figure 6g, strong adhesion was achieved on diverse metals and common plastic films, as well as on low-surface energy substrates such as PTFE (>30 kPa). The adhesion strength on glass was further compared with previously reported hydrogel surface modification strategies. Notably, previous approaches employing silica NPs [42] or 2D materials [39] as interfacial bridges showed relatively low adhesion strengths of approximately 23 and 2 kPa, respectively. Similarly, the approaches based on polymer anchoring exhibited a low adhesion strength of only ~ 6.4 kPa. These comparisons highlight that the INA strategy achieves substantially stronger interfacial adhesion compared to conventional modification methods.

To further evaluate the adhesive performance under a different loading mode, peel-off tests were additionally performed and compared with previously reported hydrogel adhesive systems (Figure S15). The INA-hydrogels exhibited peel-off adhesion forces more than three times greater than those of the corresponding pristine hydrogels, confirming the enhanced interfacial adhesion imparted by the INA treatment. Although the peel-off performance was comparable to that of several previously reported systems, the substantially higher lap-shear strengths obtained in this work suggest that the mechanically integrated INA layer is particularly effective in resisting shear deformation and promoting efficient load transfer across the hydrogel interface. These results indicate that the primary advantage of the INA strategy lies in the formation of a robust load-bearing

interface rather than solely maximizing resistance to interfacial peeling.

To further assess the applicability of INA-hydrogels in biological environments, their adhesion performance was assessed on a variety of *ex vivo* tissue substrates using a cyanoacrylate-based bioadhesive (Figure 7). When bioadhesive-treated INA-hydrogels were pressed onto porcine heart, liver, stomach, and muscle tissues, they remained firmly attached regardless of surface curvature or mechanical deformation (Figure 7a). The adhesion strength for each tissue was quantitatively evaluated using lap shear tests, revealing high adhesion strengths exceeding 20 kPa across all tissue types (Figure 7b). The failure mode was predominantly cohesive within the hydrogel, indicating that the interfacial adhesion exceeded the bulk mechanical strength of the hydrogel (Figure 7c).

Another notable advantage of the INA-based approach is its versatility and applicability to hydrogels with diverse geometries (see Figure 3f). To further exploit this capability, the INA was applied to a pyramid-structured hydrogel designed to increase the effective interfacial surface area (Figure 7d,e). The conformal formation of the interdigitated NP assembly on the 3D microstructured surface was successfully achieved without structural distortion or loss of uniformity. Owing to the increased contact area and enhanced mechanical interlocking at the interface, the pyramid-structured INA-hydrogel exhibited significantly improved adhesion performance, achieving strengths exceeding 95 kPa (Figure S16). This improvement is attributed to the increased effective contact area and stronger mechanical interlocking provided by the micro-structured interface.

The stability of the adhesive interfaces was further evaluated under prolonged exposure to aqueous environments. Both planar (2D) and pyramid (3D) structured INA-hydrogels maintained stable adhesion after more than 12 h of immersion in PBS without delamination or structural failure (Figure S17). To quantitatively assess adhesion retention under hydrated conditions, lap-shear tests were performed following 12 h of PBS immersion (Figure S18). The adhesion strengths of the planar hydrogels decreased from approximately 40–30 kPa, whereas the pyramid-structured hydrogels decreased from approximately 90–60 kPa. Despite this reduction, both systems retained substantial adhesion strength and remained mechanically integrated throughout the testing period. Notably, the 3D pyramid-structured INA-hydrogels preserved higher adhesion strength than their 2D planar structured hydrogels even after prolonged PBS immersion, highlighting the synergistic benefits of microstructural design and INA-mediated interfacial engineering. These results demonstrate that the INA strategy can be readily extended to complex 3D hydrogel architectures while maintaining robust adhesion performance under biologically relevant wet conditions.

Furthermore, the obtained adhesion performance was compared with that of commercially available tissue adhesives. Representative systems, including cyanoacrylate-, polyethylene glycol (PEG)-, and fibrin-based adhesives, typically exhibit adhesion strengths in the range of 5–15 kPa (Figure 7f), which are substantially lower than those achieved with the INA-hydrogels. In addition, the adhesion performance of the INA strategy was compared with previously reported adhesive hydrogel systems

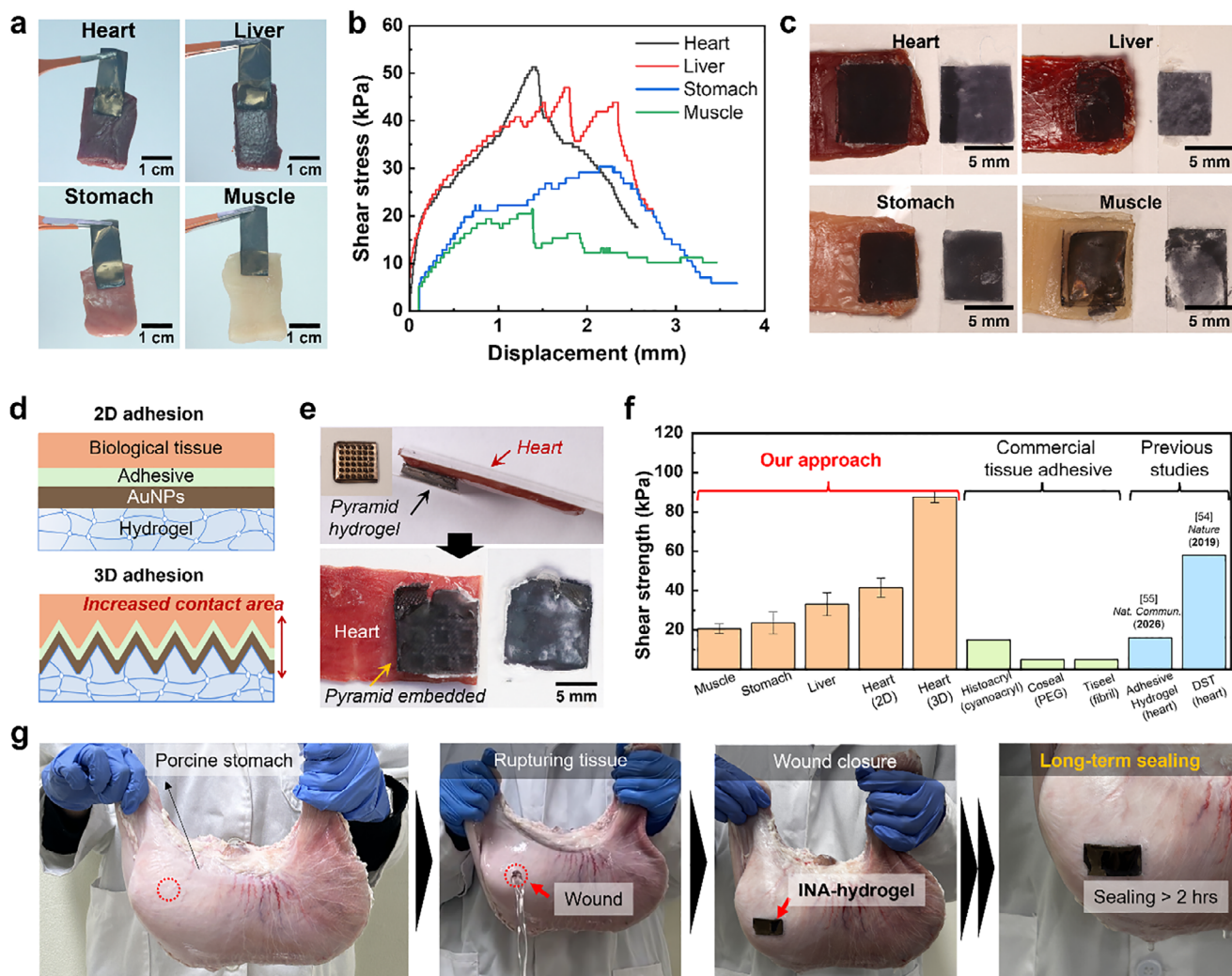


FIGURE 7 | (a) Photographic images showing bioadhesive-assisted adhesion of INA-hydrogels to various biological tissues, including porcine heart, liver, stomach, and muscle. (b) Stress-displacement curves obtained from lap shear tests of bioadhesive-treated INA-hydrogels bonded to porcine heart, liver, stomach, and muscle tissues. (c) Photographic images after lap shear testing on the respective tissues, showing cohesive failure of the hydrogel. (d) Schematic illustration comparing 2D adhesion with 3D adhesion using INA-hydrogels. (e) Photographic images of a 3D adhesion test on porcine hearts using pyramid-structured INA-hydrogel. (f) Summary of adhesion performance of the INA strategy, with comparison to commercially available tissue adhesives and previously reported adhesive hydrogels based on intrinsic chemical functionalities. (g) Photographic images showing a proof-of-concept application scenario of a bioadhesive-treated INA-hydrogel for effective sealing of liquid leakage caused by tissue perforation.

that rely on intrinsic chemical functionalities. Previously reported adhesive hydrogels, such as the dry double-sided tape (DST) system [54], achieved strong tissue adhesion through reactive functional groups, such as N-hydroxysuccinimide ester (NHS esters), which form covalent bonds with amine groups on tissue surfaces under wet conditions. This system demonstrates adhesion strengths of ~60 kPa when bonded to heart tissue. In addition, other adhesive hydrogel systems [55] incorporated enhanced adhesive moieties such as NHS esters, sulfonic acid groups, and quaternary ammonium groups at the adhesive interface. These systems facilitated interfacial bonding with biological tissues through a combination of covalent bonding, electrostatic interactions, hydrogen bonding, and dipole-dipole interactions, achieving adhesion strengths close to approximately 18 kPa on heart tissue.

Importantly, the INA approach not only matched but often surpassed the adhesion performance of these established systems, even when implemented with base hydrogels lacking inherent adhesive properties. This strategy exhibited adhesion strengths exceeding 50 kPa when bonded to heart tissue. These results highlight a key advantage of the INA strategy: strong and preferential interfacial bonding can be achieved through interfacial nano-assembly without the need for specialized adhesive chemistries or complex material design.

To further demonstrate the potential of the INA-hydrogels in biomedical applications, a proof-of-concept experiment was conducted using *ex vivo* porcine tissue models (Figure 7g). The INA-hydrogels enabled effective fluid sealing of perforated tissues. In perforated stomach models, liquid rapidly leaked through the

defects, whereas application of the INA-hydrogel with a bioadhesive produced a robust, fluid-tight seal that was maintained for more than 2 h. In addition, Live/Dead staining and CCK-8 assay results showed predominantly viable cells and a cell viability of approximately 81.5%, indicating acceptable cytocompatibility of the INA-hydrogels under the tested conditions (Figure S19). These results underscore the promise of INA-hydrogels for rapid and reliable sealing of perforated or leak-prone soft tissues using a range of bioadhesives. Overall, these findings establish INA-hydrogels as a promising class of bio-integrative sealants, capable of adhering strongly to both engineering solids and soft biological tissues, thereby enabling diverse applications in tissue repair, stabilization, and multifunctional bio-interfaces.

3 | Conclusion

In this work, we introduce a generalizable and modular interfacial engineering strategy that fundamentally redefines how hydrogel surfaces can be designed and functionalized through the formation of interdigitated NP assemblies (INAs). Based on the combined structural characterization, indirect experimental observations, and previous computational studies, the INA strategy is proposed to form through an amine-ligand-mediated ligand-exchange reaction at the hydrogel-solution interface. This process is considered to produce the assembly of AuNPs on hydrogel surfaces while simultaneously embedding into the near-surface region, thereby generating a mechanically robust interdigitated nanoscale interface with precisely tunable density and morphology. This distinctive interfacial architecture departs from conventional surface coating approaches by preserving the intrinsic bulk properties of hydrogels while imparting programmable chemical and physical functionalities to their surfaces. Moreover, the INA framework provides exceptional post-synthetic versatility. Through ligand-exchange with thiol-terminated molecular linkers, the surface chemistry and wettability of hydrogels can be spatially and deterministically controlled. Beyond molecular functionalization, the interdigitated NP layer serves as an effective interfacial nanobridge that enables the conformal integration of hydrophobic polymers—such as PTFE, PMMA, PUA, PSO, and PFPE—onto intrinsically hydrophilic hydrogel substrates. These hydrophobic polymer coatings impart pronounced anti-dehydration capability and long-term environmental stability, which can be further enhanced through silicone oil infusion, thereby overcoming one of the most persistent limitations of hydrogel-based materials.

Importantly, the hydrophobic and mechanically stable INA-engineered interface enables the effective use of commercially available adhesives that are otherwise incompatible with hydrated hydrogel surfaces. As a result, the INA-hydrogels exhibit exceptionally strong adhesion to a wide range of synthetic substrates as well as to soft and heterogeneous biological tissues, enabling robust soft-tissue sealing and fluid-tight closure under wet conditions.

Although the molecular details of the assembly process require further direct verification, the combined structural evidence, selective NP assembly behavior, spontaneous NP sintering, and agreement with previous DFT and MD studies consistently support the proposed ligand-exchange-mediated formation of

the INA architecture. Collectively, these results establish INA-hydrogels as a powerful platform for hydrogel interface engineering, integrating programmable surface chemistry, robust adhesion, environmental stability, and biological compatibility within a single modular framework. The conceptual simplicity, broad material compatibility, and interfacial versatility allow the INA strategy to be a transformative approach for next-generation hydrogel-based materials and devices, including applications in soft robotics, bioelectronics, tissue repair, and multifunctional bio-interfaces.

4 | Methods

4.1 | Materials

Ethylene glycol dimethacrylate (98%), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (98%), acrylamide (99%), N,N'-methylenebis(acrylamide) (99%), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%), tetraoctylammonium bromide (TOABr, 98%), sodium borohydride (98%), silver nitrate (AgNO_3), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), ammonium hydroxide (NH_4OH), copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), isopropyl alcohol (IPA), sodium hydroxide, 1-dodecanethiol (98%), 1-octadecanethiol (98%), 1H,1H,2H,2H-perfluorodecanethiol (97%), poly(tetrafluoroethylene) (PTFE), fluorinert FC70, and poly(methyl methacrylate) (PMMA), poly(ethyleneimine), branched (PEI, average $\text{Mw} \sim 800$ by LS, average $\text{Mw} \sim 600$ by GPC) and phosphate buffered saline (PBS, pH 7.4) were purchased from Sigma–Aldrich. Hydrochloric acid (35 wt. %–37 wt. %), toluene, *n*-hexane, sulfuric acid (95%), dimethyl sulfoxide (99%), Diethylenetriamine (DETA, 98.5%), and poly(vinyl alcohol) #500 were obtained from Samchun Chemical. Acrylic acid (99%), N-isopropylacrylamide (98%), glutaraldehyde (50% in water), tris(2-aminoethyl)amine (98%), 2-mercaptoethanol (98%), dichloromethane (99.5%, stabilized with 2-methyl-2-butene), and polyethylene glycol diacrylate ($n = \text{approx. } 9$, stabilized with MEHQ) were supplied by Tokyo Chemical Industry. Urethane acrylate prepolymer (PUA MINS 301 RM) was obtained from Minuta Technology. Perfluoropolyether (PFPE-MD700) was purchased from Junsungpolymer Co., Ltd. Silicone oil (DMS-T21, 100 cSt) was obtained from Gelest. UV-curable polysiloxane rubber (PSO, KER-4000UV) was supplied by Shinetsu.

4.2 | Synthesis of TOA-AuNPs

TOA-stabilized gold nanoparticles were synthesized using the Brust method [56]. 30 mM aqueous solution of gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) (30 mL) was mixed with a 20 mM solution of tetraoctylammonium bromide (TOABr, $[\text{CH}_3(\text{CH}_2)_7]_4\text{NBr}$) in toluene (80 mL) under vigorous stirring for more than 30 min. After phase transfer of the metal salt, the toluene phase was separated from the aqueous layer, followed by the addition of 0.4 M aqueous sodium borohydride (25 mL). The reaction mixture was allowed to react for 3 h. Subsequently, the toluene phase containing the formed gold nanoparticles was separated again and washed sequentially with 0.1 M sulfuric acid, 0.1 M sodium hydroxide, and deionized water several times.

4.3 | Synthesis of TOA-AgNPs

TOA-AgNPs in toluene were synthesized using a modified Brust-Schiffrin method. First, 9 mM of AgNO_3 in deionized water (100 mL) and 9 mM of TOABr in toluene (100 mL) were vigorously mixed for 10 min at 40°C. Subsequently, 1.44 mmol of $\text{Na}_2\text{S}_2\text{O}_3$ was added to the mixed solution and stirred until the solution became clear and transparent. After 10 min, the transparent toluene phase containing the silver precursor ions was decanted into a separate reaction flask. Then, 13.5 mM NaBH_4 , a reducing agent, in deionized water (100 mL) was slowly added to the toluene solution. After 10 min, the toluene phase with deep brown colored was separated and washed several times with 10 mM HCl and 10 mM NaOH.

4.4 | Synthesis of TOA-CuS NPs

TOA-CuS NPs were synthesized by a procedure similar to that used for the TOA-Ag NPs. Briefly, 33 mM copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water (30 mL) and 25 mM TOA in toluene (80 mL) were mixed for 15 min at 40°C, followed by the addition of 2.1 mmol $\text{Na}_2\text{S}_2\text{O}_3$. After 15 min, 9 mM of NaBH_4 was introduced to further reduce the precursors. After an additional 30 min, the deep brown toluene phase was separated and washed several times with 10 mM HCl, 10 mM NH_4OH , and deionized water.

4.5 | Preparation of poly(acrylic acid-acrylamide) (PAA-PAAm) Copolymer Hydrogel

Acrylic acid (4.8 mL), acrylamide (1.4 g), and ethylene glycol dimethacrylate (190 μL) were dissolved in deionized (DI) water (6.5 mL). Next, 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (45 mg), dissolved in dimethyl sulfoxide (300 μL) as a photo-initiator, was added to the aqueous solution. The pre-gel solution was injected into PTFE mold frames (thickness: 200 μm) sandwiched between glass slides and polymerized under UV-A irradiation (10 mW cm^{-2} , 365 nm) for 20 min. Hydrogel films were immersed in DI water for 3 days to remove residual monomers, with daily water changes.

4.6 | Preparation of poly(N-isopropylacrylamide) (PNIPAM) Hydrogel

N-Isopropylacrylamide (736 mg) and N,N'-methylenebis(acrylamide) (3 mg) were dissolved in DI water (6.5 mL), followed by the same procedure as PAA-PAAm hydrogel preparation.

4.7 | Preparation of Polyethylene Glycol Diacrylate (PEG) Hydrogel

Polyethylene glycol diacrylate was dissolved in DI water (30 wt.%). The solution (6.5 mL) was mixed with ethylene glycol dimethacrylate (190 μL), followed by the same procedure as PAA-PAAm hydrogel preparation.

4.8 | Preparation of poly(vinyl alcohol) (PVA) Hydrogel

Poly(vinyl alcohol) (0.1 g) was dissolved in DI water (1 mL) at 70°C overnight with stirring. Glutaraldehyde (125 μL) and 1.2 M hydrochloric acid (50 μL) were then added. The pre-gel solution was injected into PTFE mold frames (thickness: 200 μm) sandwiched between glass slides and allowed to polymerize for 2 h. Hydrogel films were immersed in DI water for 3 days to remove residuals, with daily water changes.

4.9 | Fabrication of 3D-Structured Hydrogel

The resin master mold was prepared using a Formlabs printer (Clear Resin V5). Following the print, the resin mold was washed in isopropyl alcohol (IPA) for 30–60 min to remove residual uncured resin, followed by UV post-curing for 1 h and thermal curing in an oven at 120°C for 1–2 h. Polydimethylsiloxane (PDMS, Sylgard 184) was poured onto the resin mold and thermally cured at 60°C–70°C. After curing, the PDMS was peeled off to obtain a negative mold for hydrogel casting. The hydrogel precursor solution was poured into the PDMS mold, and a glass slide was placed on top to form a flat surface. The setup was cured under UV light (365 nm) for 45 s. The cured hydrogel was demolded and washed in deionized (DI) water for 24 h.

4.10 | NP Assembly on Hydrogel

For the preparation of nanoparticle assembly on hydrogel, the hydrogel films were first immersed in an aqueous tris(2-aminoethyl)amine solution (TREN, 5 mg mL^{-1}) for 1 day. During this process, the films became fully swollen due to the diffusion of TREN into and onto the hydrogel network. After TREN deposition, the swollen films were gently dried using a mild air stream. The TREN-coated films were then immersed in a toluene dispersion of TOA-NPs (5 mg mL^{-1}) for a desired period, followed by washing with pure toluene to remove loosely adsorbed nanoparticles, and subsequently dried in air. During this deposition step, TOA-NPs assembled at the interface through interactions with the TREN layer on the hydrogel surface, accompanied by spontaneous room-temperature metallic sintering of the nanoparticles.

4.11 | Tape Peel-Off Test

An adhesive tape (Scotch magic tape, 3 M) was attached to the hydrogel surface. 50 g weight was placed on the tape for 1 min to ensure uniform pressure. The tape was then peeled off at an angle of 90°. To evaluate the stability of INA-hydrogel after repeated peeling, the contact angle was measured using a contact angle measurement device (DSA100, KRÜSS GmbH). A 5 μL water droplet was placed on the hydrogel surface, and the changes in contact angle were measured before and after each peeling cycle (5, 10, 20, 30, and 50 cycles). The hydrogel surface after 50 peeling cycles was observed using a field-emission scanning electron microscope (Sigma 300, Carl Zeiss, Germany).

4.12 | Ligand-Exchange on INA-Hydrogel

The ligand-exchange process was carried out by immersing the nanoparticles assembled hydrogels into precursor solutions for 10 min. The precursor solutions were prepared by dissolving thiol-terminated ligands in appropriate solvents at a concentration of 1 mol/L: 1-dodecanethiol and 1-octadecanethiol in toluene, 2-mercaptoethanol in deionized water, and 1H,1H,2H,2H-perfluorodecanethiol in dichloromethane. The resulting nanoparticles assembled hydrogels were washed with deionized water to remove residual chemicals.

4.13 | Polymer Coating on INA-Hydrogel

Stable polymer coatings on the hydrogels were conducted by spin-coating of polymer solution for 30 s at 1000 rpm. The polymer solutions were prepared by dissolving polymers in appropriate solvents at a concentration of 1 wt.%; PTFE in fluorinert FC70, PMMA in toluene, and PFPE in toluene with 0.6 M of 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photo-initiator), urethane acrylate prepolymer (pre-PUA), and polysiloxane (PSO) as is. UV-curable PFPE pre-PUA and PSO were crosslinked under additional UV-A irradiation (10 mW cm^{-2} , 365 nm) for 30 min after spin-coating. The uncoated opposite side of the hydrogel was also coated with polymers, followed by the same procedure.

4.14 | Characterization

The analysis of synthesized TOA-stabilized Au NPs was characterized by UV-vis-NIR spectrophotometer (V-770, JASCO) and field emission-transmission electron microscope (FE-TEM, JEM-F200, JEOL Ltd.). The ATR mode of Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, ThermoFisher Scientific) was conducted to demonstrate ligand exchange of nanoparticles assembled hydrogels. A sessile drop measurement instrument (DSA100, KRÜSS) was used to determine contact angles. The static contact angles were measured by dropping 10 μL of liquid on the substrate. The polymer coating on nanoparticles assembled hydrogels was characterized by field emission-scanning electron microscope (FE-SEM, JSM-7800F prime, JEOL Ltd.) and optical microscope (OM, VHX-8000, Keyence). The structure of Au NPs assembly was investigated by focused ion beam-scanning electron microscope (FIB-SEM, Helios 600, FEI) and high resolution-field emission-transmission electron microscope (HR-FE-TEM, JEM-2200FS, JEOL Ltd.).

4.15 | Adhesion Strength Measurement

Adhesion strength was evaluated by lap shear testing using a universal testing machine (NA-ST250K, Nanotech). Commercial adhesives were applied to bare hydrogels, INA-hydrogels, and partially dried INA-hydrogels (air-dried for 1 h), which were then bonded to target substrates over a defined overlap area of 10 mm $\times$ 10 mm. The assembled specimens were subjected to shear loading at a constant rate until failure. The maximum load at failure was recorded, and the adhesion strength was calculated by dividing the peak load by the overlap area. After testing, the failure mode—adhesive failure, cohesive fail-

ure within the hydrogel, or interfacial slippage—was visually examined to assess interfacial integrity. The adhesives used in this study included an epoxy-based adhesive (Vital Mix, V-tech), a cyanoacrylate-based adhesive (MXBON #23496, Cartell Chemical), and a polyurethane-based adhesive (Gorilla Glue, Gorilla Glue Company). The substrates tested included glass, polyethylene terephthalate (PET) film, polystyrene (PS) film, polyvinyl chloride (PVC) film, polytetrafluoroethylene (PTFE) film, and metal substrates (iron, copper, and aluminum). For adhesion testing on biological tissues, the same procedure was applied using porcine heart, liver, stomach, and muscle tissues as substrates.

4.16 | Cell Viability Test

Samples were sterilized under UV light for 1 h and extracted in complete DMEM at 37°C for 24 h (1 mL/cm^2). Human dermal fibroblasts (HDFs) were seeded at 2×10^4 cells/well in 24-well plates and cultured for 24 h. The medium was then replaced with DMEM containing 5% (v/v) extract and incubated for an additional 24 h. Cell viability was evaluated using a CCK-8 assay (Dojindo, Japan), and absorbance was measured at 450 nm using a microplate reader (VERSAmax, Molecular Devices, USA). Cell viability was expressed as a percentage relative to the untreated control. Live/Dead staining was performed using a Live/Dead Viability/Cytotoxicity Kit (Thermo Fisher Scientific, USA) and imaged using a confocal microscope (FV3000, Olympus, Japan).

Author Contributions

Hyeonjin Kim: conceptualization, investigation, writing – original draft, writing – review and editing, visualization, validation, methodology, formal analysis. **Woojae Chang:** conceptualization, methodology, writing – review and editing. **Yongkwon Song:** conceptualization, methodology, writing – review and editing. **Ji Min Lee:** writing – original draft, writing – review and editing, visualization, validation, methodology, formal analysis, investigation. **Atsushi Hozumi:** writing – review and editing. **Jin Yoo:** visualization, investigation, formal analysis. **Hyeseoung Lim:** conceptualization, investigation, writing – original draft, writing – review and editing, visualization, formal analysis, methodology, validation. **Sanghyuk Wooh:** conceptualization, investigation, funding acquisition, writing – review and editing, supervision, writing – original draft. **So-Jin Park:** investigation, formal analysis, visualization. **Heeyeon Kang:** validation, visualization, writing – review and editing. **Jongkuk Ko:** conceptualization, investigation, funding acquisition, writing – original draft, writing – review and editing, supervision. **Jinhan Cho:** conceptualization, investigation, funding acquisition, writing – review and editing, supervision, writing – original draft.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data supporting the findings of this study are included in the Article and Supporting Information. All data are available from the corresponding author on request.

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