

# ADVANCED MATERIALS

## Supporting Information

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### Hydrogel Paint

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#### ***Cast coating PNIPAm hydrogel pattern:***

10  $\mu\text{L}$  acetic acid ( $0.1 \text{ mol L}^{-1}$ ), 5.7  $\mu\text{L}$  silane crosslinker (TMSPMA), and 4  $\mu\text{L}$  CTA (10% volume ratio in THF) are added to every 1 mL of NIPAm aqueous solution ( $2 \text{ mol L}^{-1}$ ). Next, 2  $\mu\text{L}$  of I-2959 ( $0.1 \text{ mol L}^{-1}$  in ethanol) is added followed by an extra 10 seconds of vortex mixing. Finally, the hydrogel precursor is sealed in syringe and exposed to UV light for 30 minutes. During cure, the syringe is put on ice to keep the temperature is lower than LCST of NIPAm. After polymerization, the hydrogel paint is ready for casting. The precursor of PDMS (Sylgard 184, Dow Corning) is prepared by mixing of base and curing agent at 10:1 weight ratio. The precursor is then poured into a rectangular petri dish ( $100 \times 100 \text{ mm}^2$ ) and stored in an oven at  $65^\circ\text{C}$  for 12 hours. The cured PDMS sheet with thickness of 2 mm is cut into  $40 \times 40 \text{ mm}^2$  pieces. Before casting p(NIPAm-co-TMSPMA) hydrogel paint, the surface of the PDMS sheet is treated by oxygen plasma (SPI Plasma Prep II) for 3 minutes to introduce hydroxyl groups on the PDMS surface. A 1.5-mm-thick acrylic mold with a butterfly-shaped hollow pattern is placed on the surface of the as-treated surface of PDMS. Before casting hydrogel paint into the mold, the pH of the paint is tuned to 1 by hydrochloric acid to accelerate the curing and bonding formation of the hydrogel paint. After the casting, we use another acrylic sheet to cover the hydrogel paint. After storing for 2 hours at room temperature, the PNIPAm hydrogel paint cures and chemically bonds

to the PDMS sheet. Note that due to the intrinsic thermo-responsive property of the PNIPAm, the samples are cured at room temperature to avoid phase separation.

***Spin coating PAAc hydrogel on PDMS:***

P(AAc-co-TMSPMA) hydrogel paint is synthesized in the following condition: For 1-mL of acrylic acid aqueous solution ( $2 \text{ mol L}^{-1}$ ),  $10 \text{ }\mu\text{L}$  of CTA (1% v/v in THF),  $5.7 \text{ }\mu\text{L}$  of silane crosslinker (TMSPMA) are added, followed by vortex-mixing for 60 s. Then,  $2 \text{ }\mu\text{L}$  of I-2959 ( $0.1 \text{ mol L}^{-1}$  in ethanol) is added followed by additional mixing for 10 s. The resulting transparent solution is sealed in a plastic syringe and subject to UV irradiation. After 30 min of UV irradiation, the p(AAc-co-TMSPMA) hydrogel paint is obtained. Sylgard 184 is used to produce PDMS film (Base : crosslink agent = 10:1 by weight). The as-prepared PDMS film is subject to oxygen plasma treatment for 3 minutes to graft hydroxyl groups. The hydrogel paint is casted on the plasma-treated PDMS film fixed on a spin-coater (SU-8 Spin Coating Station, Reynolds Tech). The spinning coating process proceeded for 60 s. Changing the spinning rate (from 500 to 3000 rpm) results in polymer solution with various thicknesses. The resulting film is put in a small humid container and stored in oven at  $65^\circ\text{C}$  for 24 hours.

***Brush coating PAAm hydrogel on model boat:***

For every 1 mL of AAm solution ( $2 \text{ mol L}^{-1}$ ),  $1.9 \text{ }\mu\text{L}$  of TMSPMA,  $10 \text{ }\mu\text{L}$  of acetic acid solution ( $0.1 \text{ mol L}^{-1}$  in water) and  $1 \text{ }\mu\text{L}$  of CTA solution (1%v/v in THF) are added. After one-minute stirring of the mixture by vortex,  $2 \text{ }\mu\text{L}$  of I-2959 solution ( $0.1 \text{ mol L}^{-1}$  in ethanol) is added and followed by 10 seconds vortex mixing. The hydrogel precursor is sealed in syringe and exposed to UV for 30 minutes. After the polymerization, the hydrogel paint is ready for use. The skeleton

of the home-made boat model is made of PET film and its exterior is covered by aluminum tape. Before brush-painting hydrogel paint on the boat hull, we conduct oxygen plasma treatment on it for 3 minutes to make it hydrophilic and maximize surface hydroxyl group density. The hydrogel paint is brush-painted to the boat hull and then the boat is sealed in a small humid container, which is then subject to oven heating at 65°C for 24 hours.

#### ***Adhesion of hydrogel coating on various substrates:***

We cast hydrogel paint on various substrates to form a hydrogel coating with 60 mm length, 20 mm width and 1.5 mm thickness. The casted hydrogel paint is cured by stored in oven with 65°C for 24 hours. Then the adhesion energy is measured by the 90-degree peel test. The peeling rate is fixed at 10 mm min<sup>-1</sup>. The recipe of the hydrogel coating is as follows: for every 1 mL of 2 M AAm, we add 10 µL of acetic acid solution (0.1 M), 1.9 µL TMSPMA, 1 µL (1% v/v in THF) CTA solution and 2 µL I-2959 solution (0.1 M in ethyl alcohol). The substrates we use are the following: nitinol, aluminum, steel, glass (silica) and ceramic (macor) substrates are rinsed by ample DI water and blown dry by nitrogen flow, no oxygen plasma treatment is needed before applying hydrogel paint. PDMS surface is treated by oxygen plasma for 3 minutes. For plastic, we use polystyrene sheets, which are treated by oxygen plasma for 10 minutes before applying hydrogel paint.

#### ***Stability of hydrogel coating in PBS:***

The hydrogel paint with the same recipe as that is used for dipping nitinol guidewires, is casted on a clean nitinol substrate. After being stored in oven at 65°C for 24 hours, the hydrogel paint cures and a hydrogel coating with dimension of 60 mm in length, 20 mm in width and 0.3

mm in thickness forms on the substrate. Next, the hydrogel coated nitinol substrate is immersed in PBS for 7 days. Adhesion between hydrogel coating and substrate is checked daily to evaluate the stability of hydrogel coating in PBS.

***Contact angle measurement:***

A water tank with an opening on the top surface is assembled using glass slides and hot glue. During measurement, the tank is filled up with water, and the aluminum boat is placed on water surface. Using contact angle measuring system (homemade contact angle measuring system at the courtesy of Dr. Arthur McClelland at the Center for Nanoscale Systems, Harvard University), clear image at the boat bottom underwater can be captured. A drop of mineral oil (with the volume of  $\sim 10 \mu\text{L}$ ), is deposited onto the boat bottom through a U-shaped needle tip connected to a syringe. The images are taken sideview after the oil drop became stationary. The contact angle is measured using the software Image-J. For each data point, at least five contact angles are taken to obtain a mean value.

***Preparation of powder products:***

To explore the possibility to extend shelf life of hydrogel paint, we design a strategy to nearly pause the silane condensation by freeze drying. Typically, the hydrogel paint is prepared according to experimental section. The as-prepared hydrogel paint is subject to freezer at  $-80^\circ\text{C}$  overnight. The resulting frozen hydrogel paint is put in lyophilizer (VirTis AdVantage Plus EL - 85), which is set at  $-20^\circ\text{C}$  at high vacuum for 1 week to completely remove water. The hydrogel paint becomes white porous solid, which is then grinded into fine powder and store in sealed

container for further use. Upon each usage, certain amount of powder is dissolved in DI water to obtain hydrogel paint.

***Preparation of non-interlinked hydrogel coating on guidewire:***

The clean nitinol guidewire is treated with oxygen plasma, followed by silane modification with aminopropyltrimethylsiloxane. The purpose for the silane modification is to both hydrophilize guidewire surface and fully occupy the surface hydroxyl groups so that the silane groups in hydrogel paint cannot interlink to the guidewire surface anymore. The modified guidewire is immersed in hydrogel paint prepared according to the experimental section. And the dip coating procedure is also base on the description in experimental section.

**Supporting movies:**

**Movie S1.** Dip coating PAAm hydrogel paint on nitinol guidewire surface. The guidewire is drawn out from the pool of hydrogel paint by the Instron control unit at a velocity of 10 mm min<sup>-1</sup>.

**Movie S2.** Swelling of dried PAAm hydrogel coating on nitinol guidewire surface. The hydrogel coating on the wire is produced based on hydrogel paint. When exposed in dry air, the hydrogel coating is barely visible under the microscope. When immersed in water, the hydrogel coating swells and reaches swelling equilibrium in less than 1 second. As time further elapses, the coating thickness remains the same and its surface is smooth, indicating that the hydrogel coating is stable over time.

**Movie S3.** Temperature responsiveness of p(NIPAm-to-TMSPMA) hydrogel pattern coated on PDMS surface. The as-prepared hydrogel butterfly pattern resides on the PDMS sheet. Then the PDMS sheet is immersed between cool (22°C) and warm (46°C) water, alternatively. The pattern repeatedly reveals in warm water, and disappears in cool water, which indicates that the thermal-responsive hydrogel coating is stably adhering to PDMS surface during the cyclic immersion and cyclic phase transition processes.

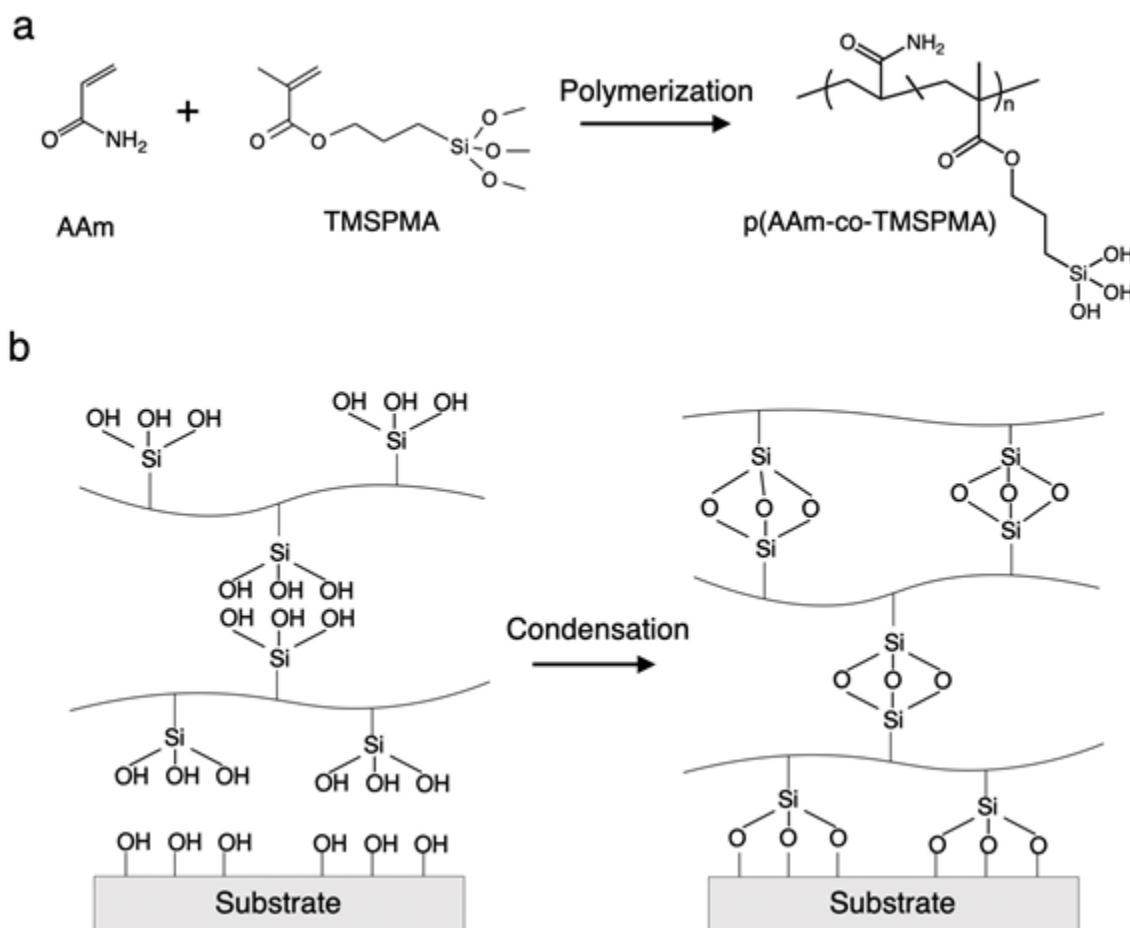
**Movie S4.** The rolling up motion of p(AAc-co-TMSPMA)/PDMS bilayer. At pH = 14, the hydrogel adsorbs water, appearing to be transparent and swollen, while the PDMS does not. With covalent bonding between the hydrogel layer and PDMS layer, the swelling of hydrogel forces PDMS to bend. As a result, the bilayer rolls up.

**Movie S5.** The unrolling motion of p(AAc-co-TMSPMA)/PDMS bilayer. At pH = 1, the hydrogel repels water, appearing to be milk-white and deswelling. With the strong bonding, the bilayer unwinds to regain its original shape.

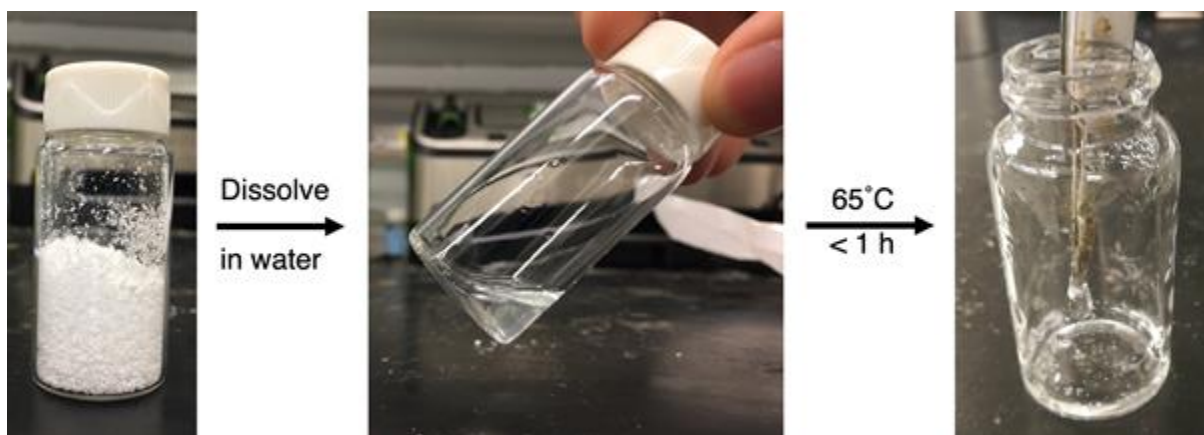
**Movie S6.** The PAAm hydrogel paint is deposited on the surface of a yellow paper. The boat is made of a pre-cut PET sheet and wrapped up by aluminum tape. In the movie, the hydrogel paint is brush-painted and cured on the exterior boat hull.

**Movie S7.** The contact angle measurement of drops of mineral oil on p(AAm-co-TMSPMA) hydrogel coated boat bottom underwater.

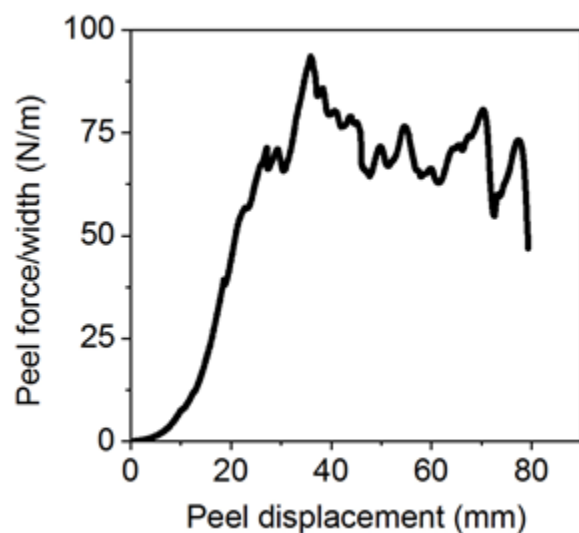
**Movie S8.** Coated and uncoated boats floating on mineral-oil-covered (stained by oil red) water surface. The uncoated boat is contaminated by the oil upon direct contact. By contrast, the p(AAm-co-TMSPMA) hydrogel coated boat breaks up and repels the oil, revealing strong anti-contamination function for the marine vessels and facilities.



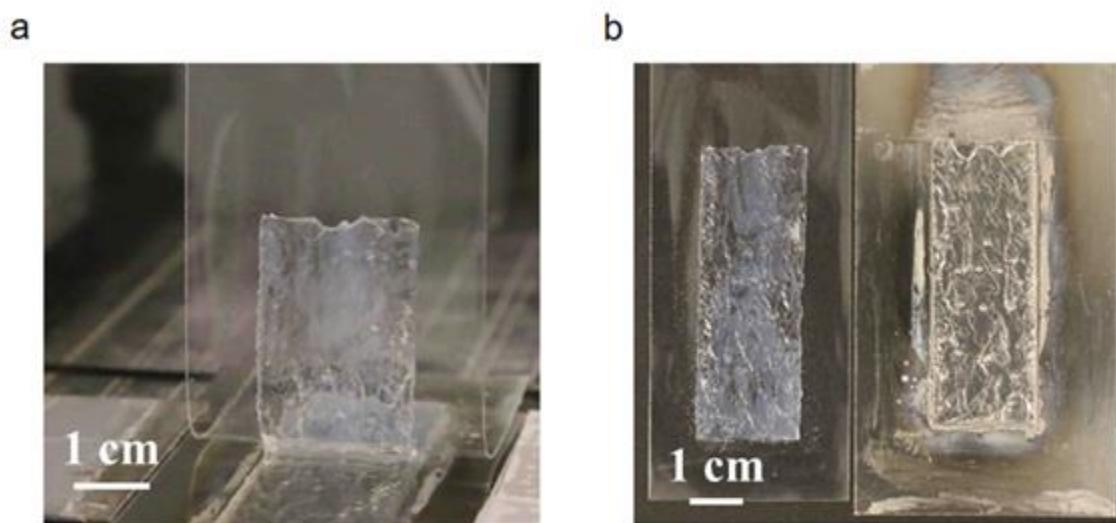
**Figure S1.** An example of hydrogel paint. a) During formulation, a species of monomer (acrylamide) and a species of silane coupling agent (TMSPMA) copolymerize into polymer chains, without crosslinking into a polymer network. Silane hydrolyzes into silanol. b) The surface of a substrate has hydroxyl groups. During cure, the silanol groups condense with each other to crosslink the polymer chains into a polymer network, and condense with the hydroxyl groups to interlink the polymer network to the substrate.



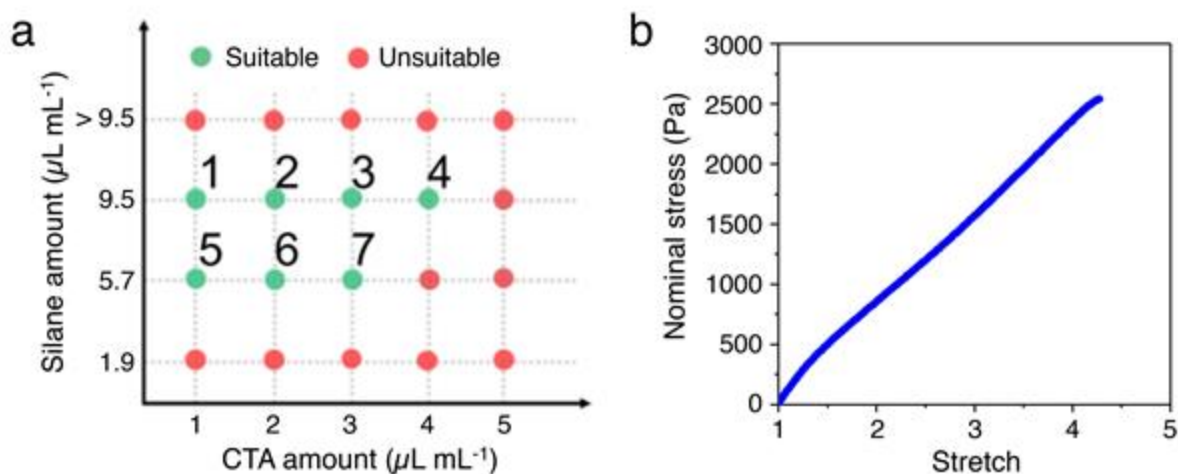
**Figure S2.** After polymerization, the hydrogel paint can be dried, ground into powders, and stored. After re-dissolving in water, the hydrogel paint cures to crosslink the polymer chains into a polymer network, and interlink the polymer network to a substrate.



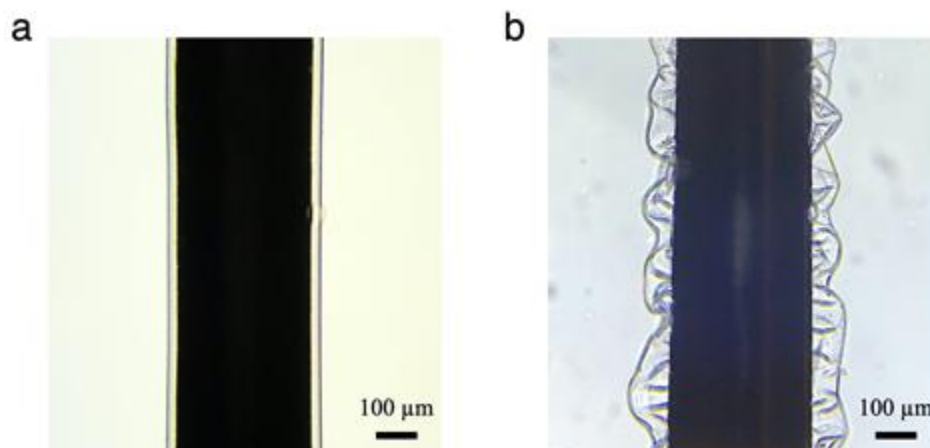
**Figure S3.** A typical force-displacement curve of a peel test. The adhesion energy is the force at steady state (in this case is the average force between 40-80 mm of displacement) divided by the width of the sample.



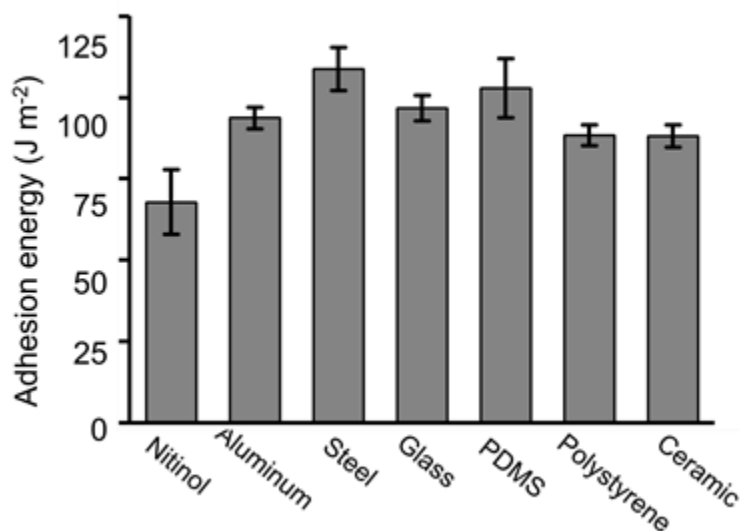
**Figure S4.** a) Cohesive fracture of hydrogel coating on a nitinol substrate. b) After peeling, hydrogel residues are left on both the backing layer and nitinol substrate. The hydrogel is identical to that for dipping nitinol guidewires.



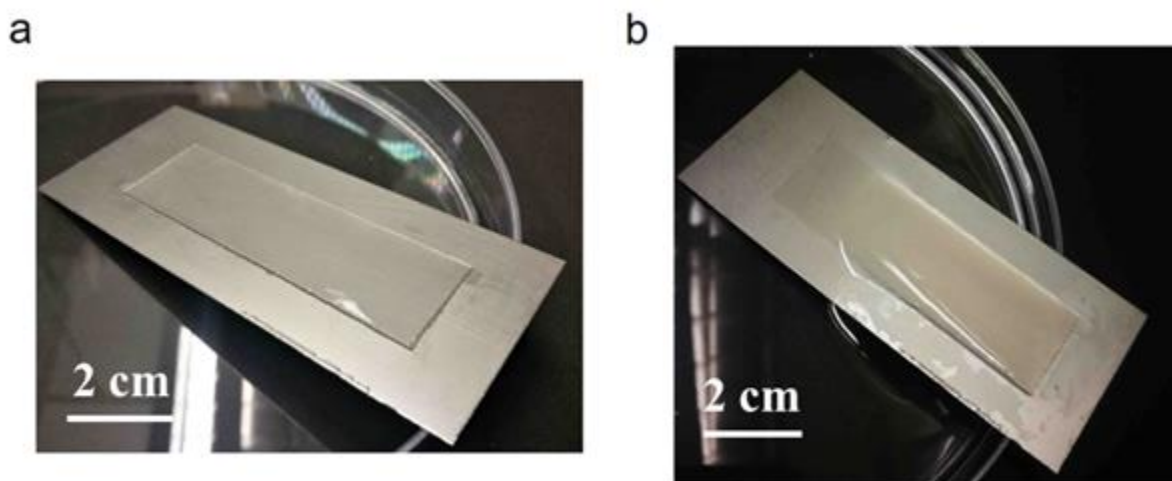
**Figure S5.** P(AAm-co-TMSPMA) hydrogel paint for nitinol guidewire. a) Diagram showing the feasible (green dots)/infeasible (red dots) recipes for dip coat. The feasible criteria are set as following: after polymerization under UV for 30 minutes, the hydrogel paint should remain as a liquid to allow dip-coat. Then, after curing at  $65^{\circ}\text{C}$  for 24 hours, the hydrogel paint should be able to solidify. Too much silane makes the hydrogel paint too viscous to dip-coat after polymerization, while too much CTA makes the hydrogel paint liquid after cure. b) One representative tensile stretch-stress curves of the bulk hydrogel sample (50 mm in width, 3 mm in thickness and 10 mm in height) prepared from Recipe 5. Three sample are stretched along the height direction with a constant speed of  $100\text{ mm min}^{-1}$ . The rupture stretch is  $4.25 \pm 0.24$ , strength  $2.17 \pm 0.35\text{ kPa}$ , and shear modulus  $238.1 \pm 52.5\text{ Pa}$  (one fourth of initial slop of stretch-stress curve).



**Figure S6.** Hydrogel-coated nitinol guidewire a) with siloxane interlinks, and b) without siloxane interlinks.



**Figure S7.** Adhesion of hydrogel coating on various substrates. In all cases, cohesive failure is observed, implying that strong adhesion is formed. The error bars for each substrate are obtained from at least three samples. Metals including nitinol (from Innomed Ltd. Co., China), aluminum, steel (from McMaster-Carr) as well as oxides (silica and macor, both from McMaster-Carr) are used without surface treatment. Elastomer (PDMS, Sylgard 184, Dow Corning) and plastic (polystyrene, VWR) are treated by oxygen plasma for 3 minutes and 10 minutes before applying hydrogel paint, respectively.



**Figure S8.** Stability of hydrogel coating on nitinol substrate in PBS. a) Hydrogel coating forms on nitinol substrate by casting. The hydrogel coating bonds on the nitinol substrate without delamination before immersed in PBS. The hydrogel coating has a dimension of 60 mm in length, 20 mm in width and 0.3 mm in thickness. b) After immersed in PBS for 7 days. The

hydrogel coating slightly swells but still bonds tightly to the nitinol substrate without delamination.

**Table S1.** The choice of polymers and the corresponding performances.

pH responsive	Poly(acrylic acid), boronic acid*	[1]
Thermal responsive	Poly(N-isopropylacrylamide), poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide)	[2]
Light responsive	Spiropyran* Azobenzene*	[3], [4]
Anti-thrombus/hemo-compatibility	Poly(zwitterions) Poly(ethylene glycol), Poly(hydroxyethyl-methylacrylamide)	[5], [6]
Anti-fouling	Poly(acrylamide), Poly(ethylene glycol)	[7]
Biodegradation	Poly(ethylene glycol), alginate, chitosan, gelatin (GelMa)	[8-10]
Self-healing	Xanthan gum, boronic acid, clay and silicon particle	[11]

\*These substances are not polymers but rather, functional groups that can be imparted to monomers or polymer chains by well-known chemistries.

### Supporting References

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