

Supporting Information for:

Redox Responsive Release of Hydrophobic Self-Healing Agents from Polyaniline Capsules

Li-Ping Lv,[†] Yi Zhao,[†] Nicole Vilbrandt,[‡] Markus Gallei,[‡] Ashokanand Vimalanandan,^{||} Michael Rohwerder,^{||} Katharina Landfester,[†] and Daniel Crespy^{*,†}

[†] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

[‡] Ernst-Berl Institute for Chemical Engineering and Macromolecular Science, Darmstadt University of Technology, Petersenstrasse 22, 64287 Darmstadt, Germany

^{||} Max Planck Institute for Iron Research GmbH, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany

* crespy@mpip-mainz.mpg.de

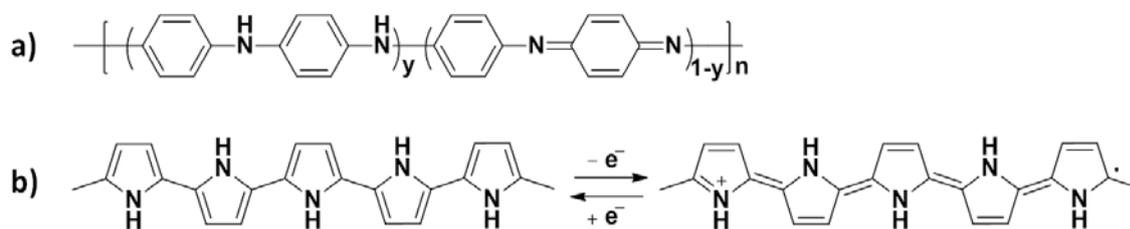


Figure S1. Oxidation states of **a**: polyaniline (depending on y); **b**: polypyrrole.

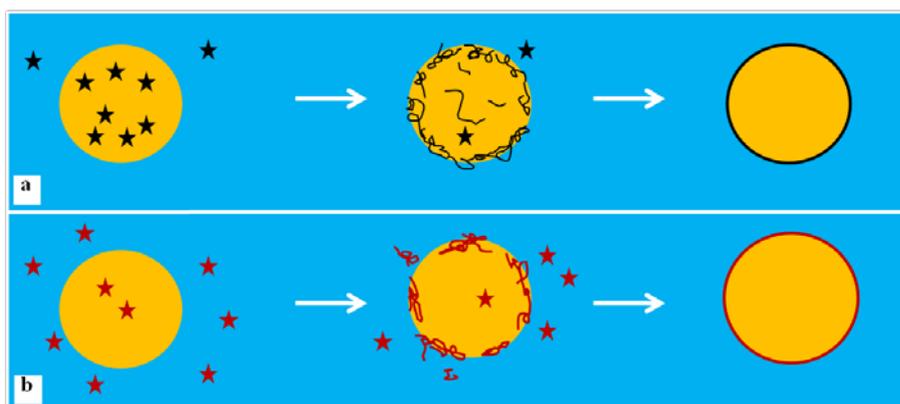


Figure S2. Schematic representation of the polymerization reaction of the monomers (stars) in the case of **a**: the aniline, **b**: the pyrrole monomer.

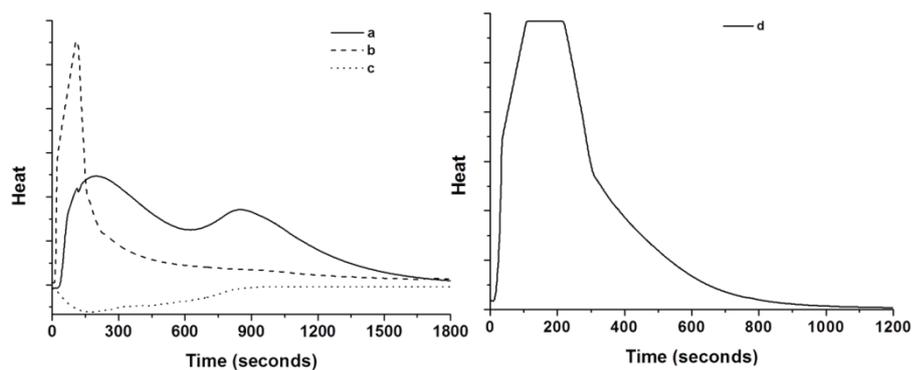


Figure S3. Calorimetric thermograms of the polymerization of **a:** aniline in miniemulsion; **b:** aniline in DMSO; **c:** control measurement with aniline in miniemulsion and water added instead of APS aqueous solution; **d:** pyrrole in miniemulsion.

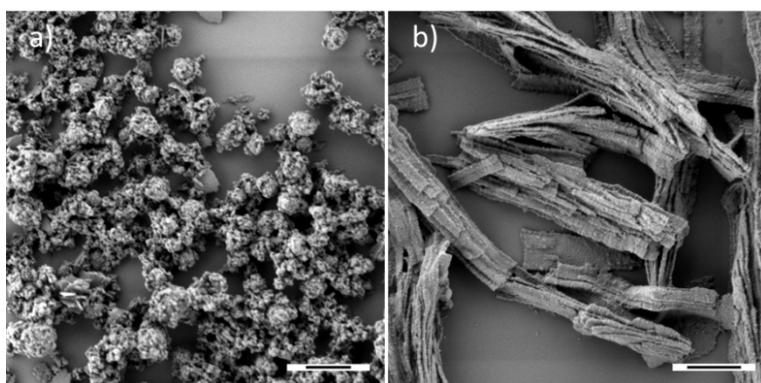


Figure S4. SEM micrographs of PANI prepared with different stabilizers **a:** SDS and PVP K30; **b:** Lutensol AT50 and PVP K30. The scale bars represent 1 μm .

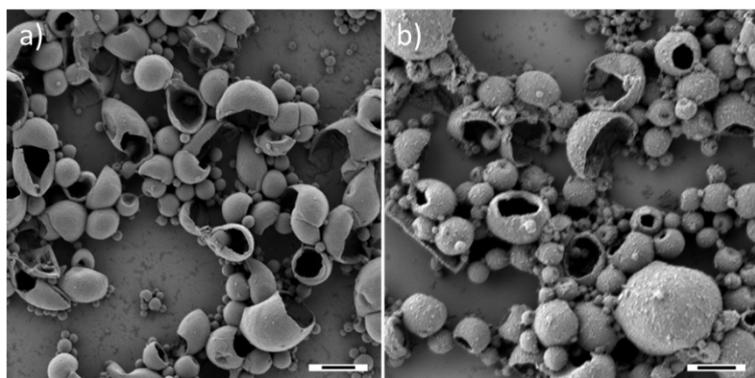


Figure S5. SEM micrographs of PANI prepared under different temperature **a:** RT; **b:** 0 $^{\circ}\text{C}$. The scale bars represent 1 μm .

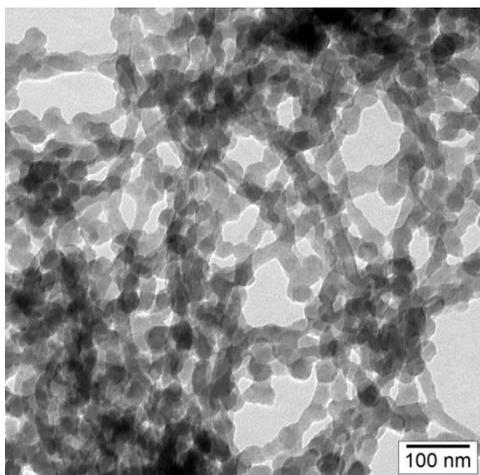


Figure S6. TEM micrograph of PPy nanoparticles (PPy-3). The nanoparticles were prepared at RT with an initial ratio Py:EB=96:4 (v:v).

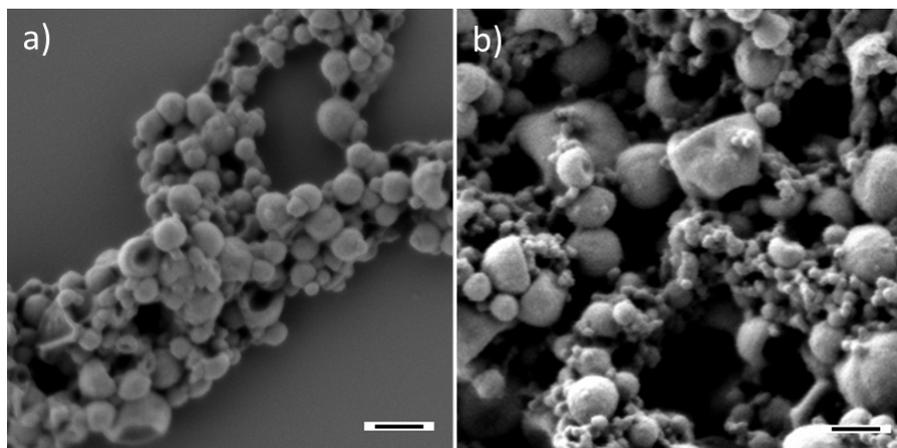


Figure S7. SEM micrographs of PPy prepared under different temperature **a:** 0 °C; **b:** RT. The scale bars represent 200 nm.

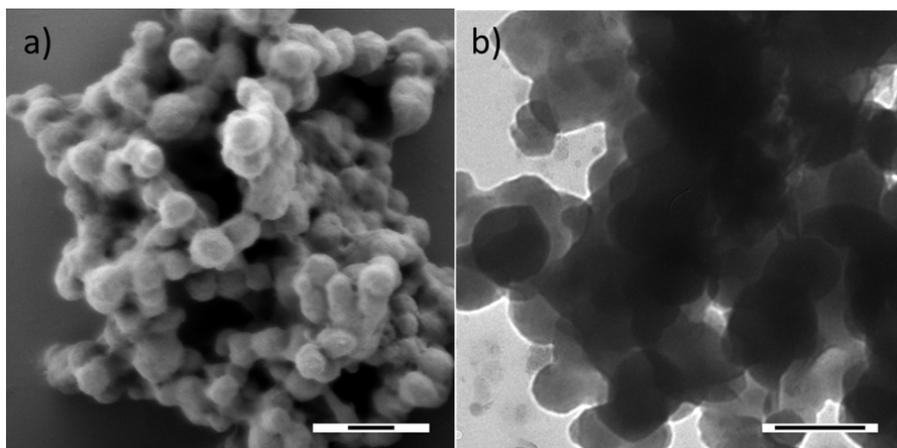


Figure S8. SEM and TEM micrographs of PPy prepared with the feed ratio of Py:EB=30:70 (v:v). The scale bars represent 200 nm.

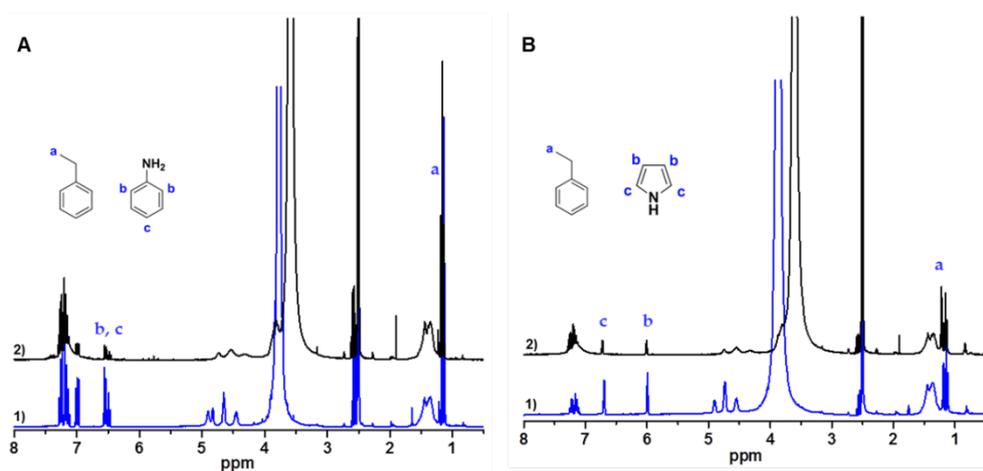


Figure S9. ¹H NMR spectra of PANI-1 (A) and PPy-1 (B) dispersions before (1) and after (2) polymerization.

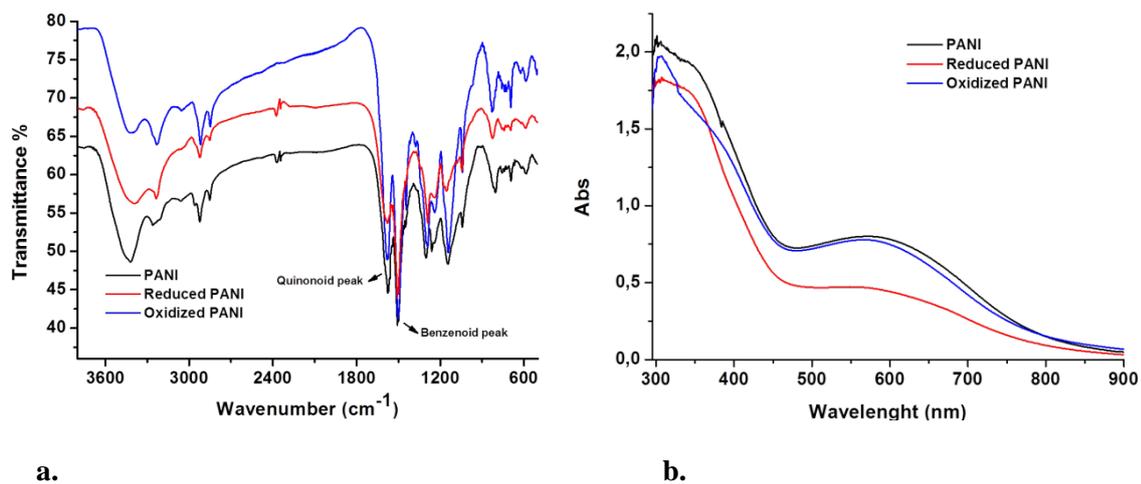


Figure S10. a: FT-IR spectra of purified PANI-1 before and after reduction or oxidation by N_2H_4 or H_2O_2 aqueous solutions for 12 h. The molar ratio of ANI unit to N_2H_4 or H_2O_2 was 1:43. **b:** UV-vis spectra of purified PANI-1 in NMP before and after reduction or oxidation by N_2H_4 or H_2O_2 aqueous solution for 12 h. The molar ratio of ANI unit to N_2H_4 or H_2O_2 was 1:43.



Figure S11. Photographs of $0.1 \text{ mg}\cdot\text{mL}^{-1}$ of PANI in NMP after addition of water (control), H_2O_2 (oxidized) and N_2H_4 (reduced) after 12 h.

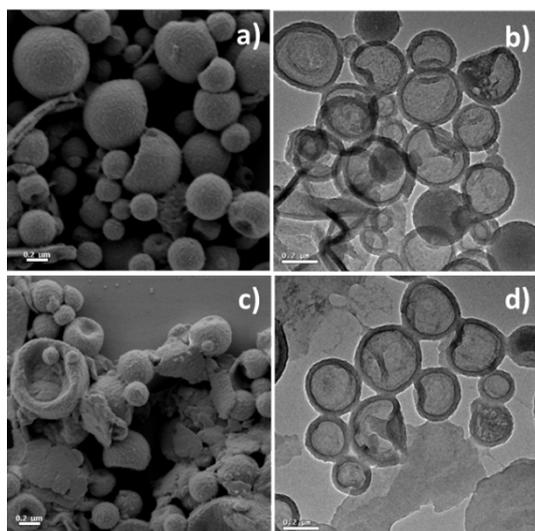


Figure S12. SEM and TEM micrographs of purified PANI-1 after oxidation (a-b) or reduction (c-d) by H_2O_2 or N_2H_4 aqueous solution for 12 h. The molar ratio of ANI unit to N_2H_4 or H_2O_2 was set as 1:43.

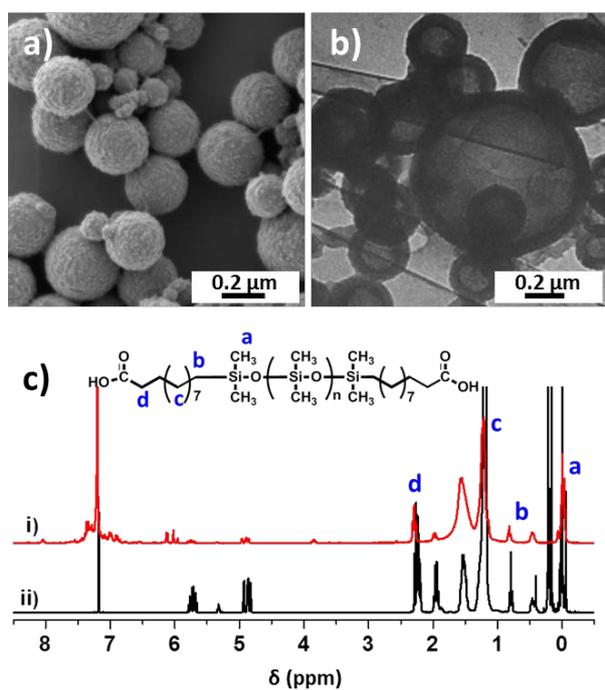


Figure S13. **a:** SEM and **b:** TEM micrographs of PANI/PDMS-DC capsules after purification. **c:** ^1H NMR spectrum of **i)** PANI/PDMS-DC capsules after purification, drying, grinding and dissolution of the PDMS-DC in CDCl_3 and **ii)** pure PDMS-DC.

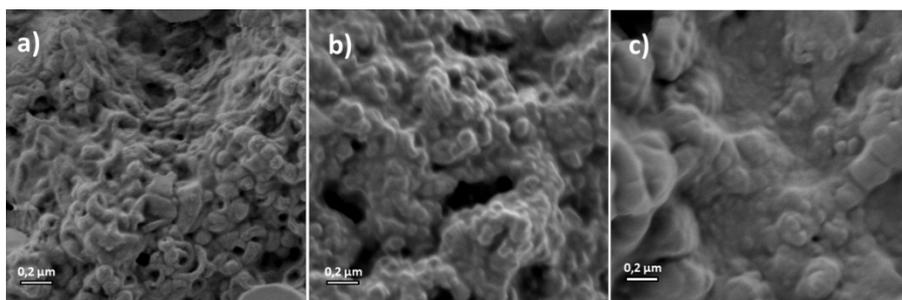


Figure S14. SEM micrographs of purified PANI/PDMS-DE dispersed in THF before (a) and after oxidation (b) or reduction (c) by H_2O_2 or N_2H_4 aqueous solutions for 12 h. The molar ratio of ANI unit to N_2H_4 or H_2O_2 was set as 1:43.

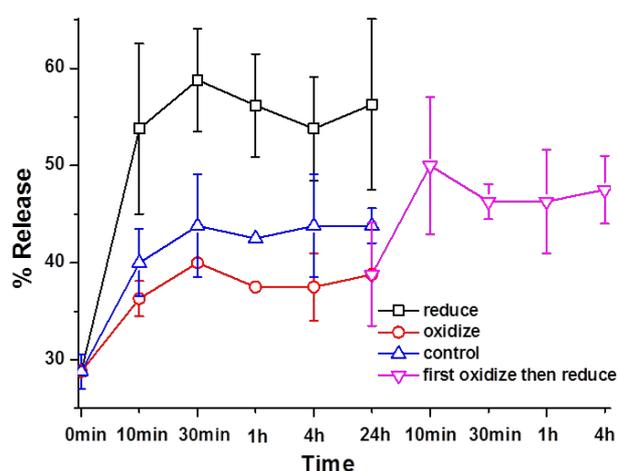


Figure S15. Release of PDMS-DC from PANI capsules under different conditions. In the control experiment, the same volume of solvent and reactants were used but without oxidizing or reducing agents.

Incorporation of the capsules in polymer coatings

Incorporation of the capsules in PVA films

Certain amounts of purified PANI/PDMS-DC capsule dispersions (4 wt.% of PANI + PDMS-DC) were first mixed with a 9 wt.% aqueous solution of PVA and then stirred for 3 min with a vortex. The ratio of PANI + PDMS-DC to PVA was 1 wt.%. Then the mixture was casted to form a 1.5×3 cm film on a microscope slide and dried under room temperature. To determine the stability of capsules in

PVA matrix after the formation of film, the PVA matrix was removed by immersing the film in water for 12 h. Then the capsules were collected by centrifugation and the morphology was studied by AFM. Some non-purified capsules were also freeze-dried and the amount of remaining PDMS-DC was determined by ^1H NMR in $\text{THF-}d_8$ (pyrene as internal standard) after dissolving the capsules in NMP/DMSO: 1/1 vol/vol.

The amount of PDMS-DC in the recovered capsules was quantified by ^1H NMR spectroscopy and compared to the amount present in the capsules prior to embedding in PVA films. 88% of PDMS-DC could be recovered. Comparing this value with the encapsulation efficiency of 89% indicates that only a minor leakage ($\sim 1\%$) of the self-healing agents from the inner core of the capsules occurred.

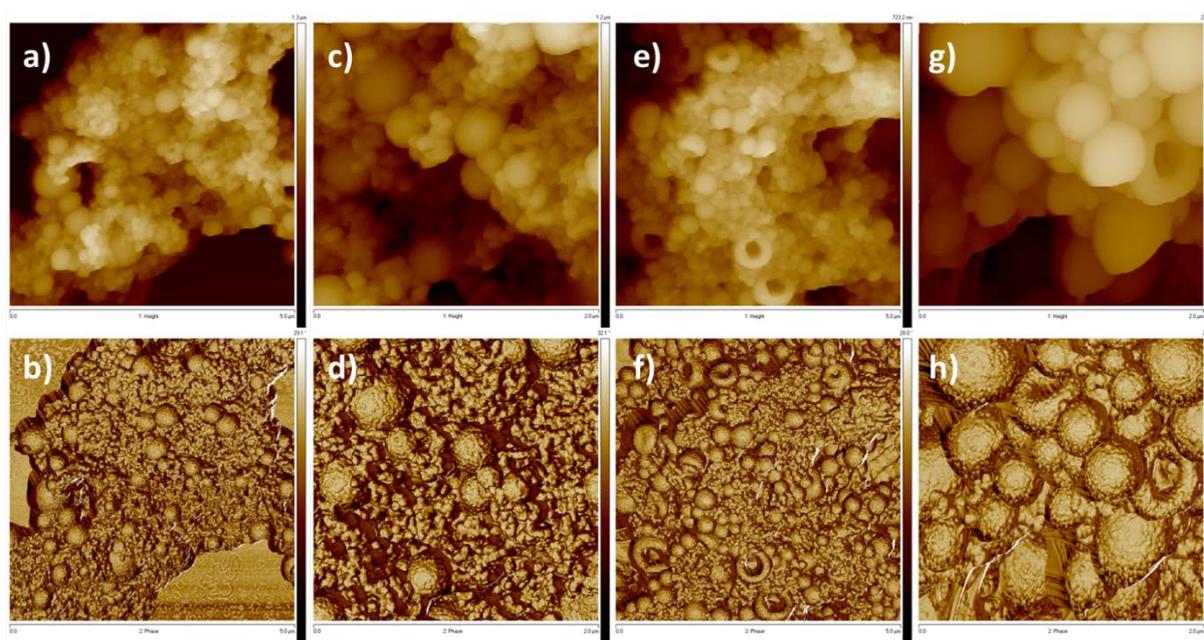


Figure S16. AFM height (a, c, e, g) and phase (b, d, f, h) images of the PANI/PDMS-DC capsules before (a, b) and after (e, f) embedding in PVA film. The scales represent $5\ \mu\text{m}\times 5\ \mu\text{m}$. (c, d) and (g, h) are the magnification images ($2\ \mu\text{m}\times 2\ \mu\text{m}$) of samples a) and e), respectively.

Incorporation of the capsules in hydrophobic acrylate coatings

Synthesis of the dispersion for the acrylate coating

A mixture of MMA (2.13 mL, 0.02 mol), BA (2.25 mL, 0.02 mol), and hexadecane (0.194 mL, 0.66 mmol) was added to 16 mL of water containing 100 mg of Lutensol AT 50 and 10 mg KPS. After stirring under 1000 rpm for 1 h at room temperature, the mixture was ultrasonicated for 120 s at 70% amplitude (Branson sonifier W450) under ice cooling. Before polymerization, the miniemulsion

dispersion was degassed with Ar for 10 min. Then the reaction was carried in an oil bath under 72 °C for 20 h. After polymerization, a dispersion of P(MMA-*co*-BA) nanoparticles with a solid content of 20 wt.% was obtained.

Preparation of the capsules/acrylate coatings

50 μL of purified PANI/PDMS-DC dispersion (4 wt.% of PANI + PDMS-DC) was mixed with 50 μL of the acrylate dispersion (20 wt.%) and stirred for another 1 h. The ratio of PANI + PDMS-DC to P(MMA-*co*-BA) was \sim 20 wt.%. Then 40 μL of the mixed dispersion was casted on a 2×2 cm silicon wafer and dried under room temperature. To observe the SEM cross section images of the film, the as-prepared silicon wafers with capsules-embedded P(MMA-*co*-BA) film were first immersed into liquid nitrogen for 3 min and then quickly broken by tweezers. For the SEM-EDX measurements, the films were prepared on a thick carbon conductive tape instead of silicon wafer to eliminate all the signals of silicon from the substrate.

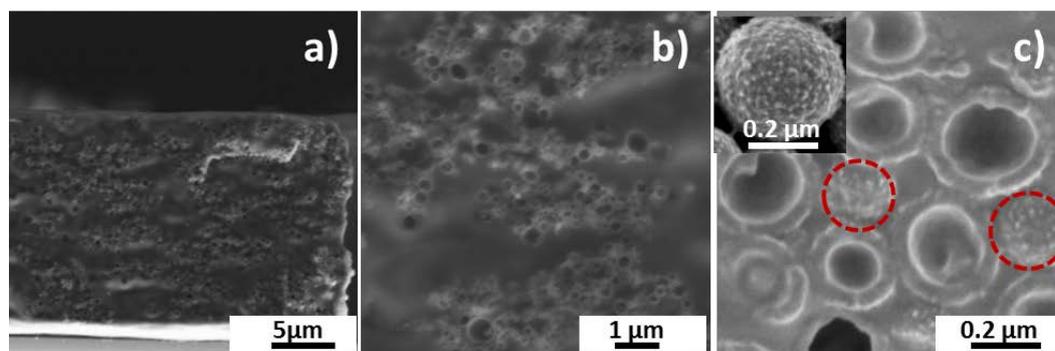


Figure S17. SEM cross-section micrographs of hydrophobic acrylate coatings with embedded PANI/PDMS-DC capsules. The inset image in c) displays the surface of a PANI/PDMS-DC capsule prior to embedding in the acrylate coating, showing its similarity with the capsules remaining in the sectioned coating (red circles).

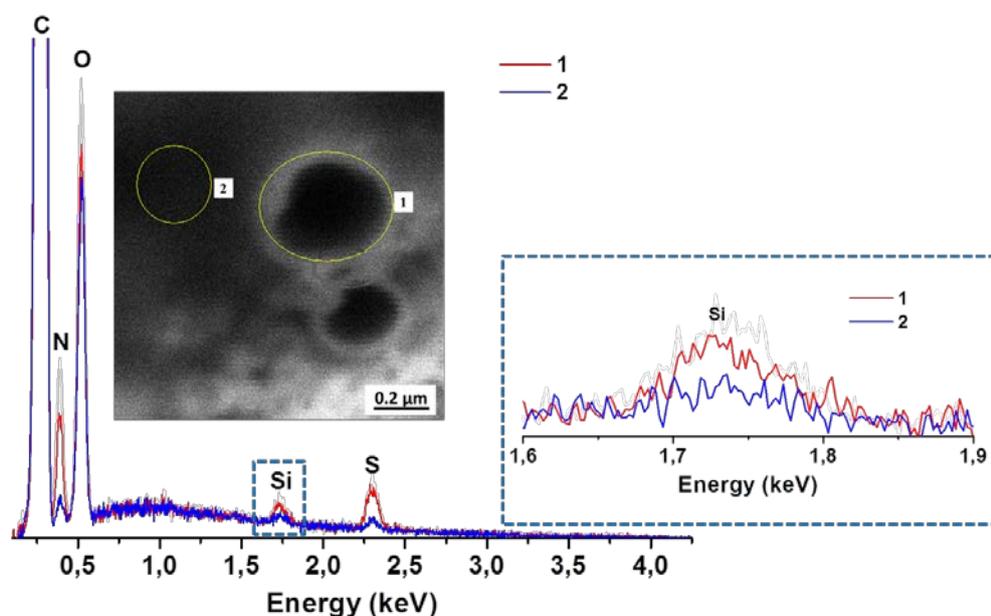


Figure S18. SEM-EDX spectra of PANI/PDMS-DC capsules embedded in the hydrophobic acrylate coating. The spectrum 1 is taken on a capsule (area 1) whereas the spectrum 2 is taken near the capsule (area 2), *i.e.* on the matrix. The Si signal from PDMS is detected in the area 1, indicating that the PDMS is encapsulated in the PANI containers that are embedded in the acrylate coating.

Deposition of the capsules/acrylate coating on a zinc plate

Purified PANI/PDMS-DE (2.4 wt.% of PANI + PDMS-DE) or PANI/PDMS-DC (4 wt.% of PANI + PDMS-DC) capsules dispersion were first mixed with the P(MMA-*co*-BA) dispersion (20 wt.% solid content). The weight ratios of capsule dispersion to polymer dispersion in the above mixtures were around 50:50 and 70:30, respectively. Then 80 μ L of each mixture was casted onto the surface of a zinc foil (1cm \times 2 cm, grinded with grinding paper, cleaned by ultrasonication in THF then ethanol for 5 min, rinsed with distilled water and dried under Argon). After drying at room temperature, a capsules/acrylate coating was formed on zinc. The zinc foil was then cut with a scissor and polished by using Hitachi cross-section polisher (ion milling machine). The EDX spectra were taken with an SEM (Zeiss LEO 1550 VP).

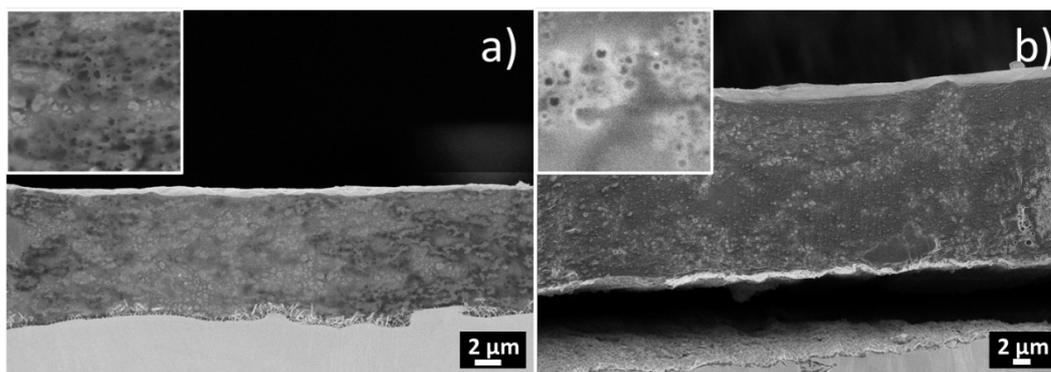


Figure S19. SEM micrographs of cross-sections of the acrylate coating on zinc with incorporated **a:** PANI/PDMS-DE; **b:** PANI/PDMS-DC.

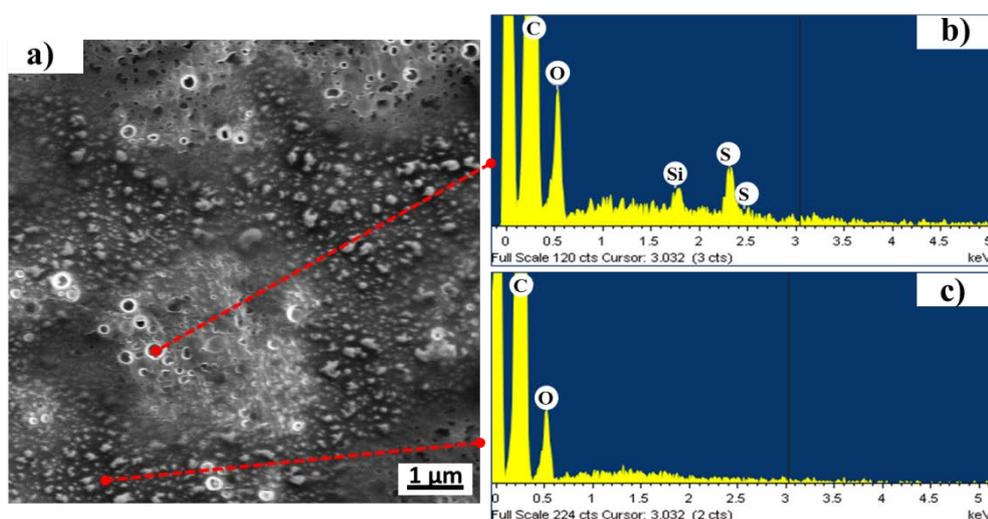


Figure S20. a: SEM cross-section image of the PANI/PDMS-DC capsules/acrylate coating on a zinc foil. **b:** EDX spectrum of one capsule (indicated with a red dot) in the coating. **c:** EDX spectrum of the matrix (indicated with another red dot).