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Supporting Information

Room-temperature healable, recyclable and mechanically super-strong poly(urea-urethane)s cross-linked with nitrogen-coordinated boroxines

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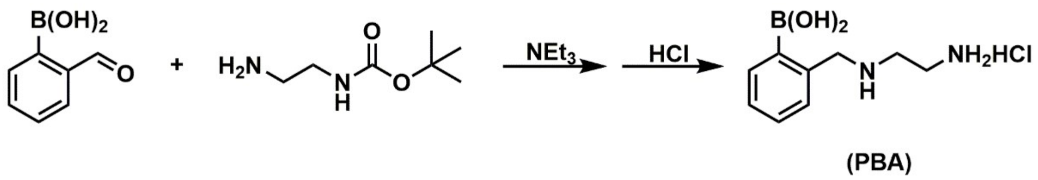
Characterizations: ^{1}H NMR spectra were taken on a 500 MHz Bruker instrument. FT-IR spectra were measured by using VERTEX 80 V FT-IR spectrometer. The UV-Vis transmission spectrum was taken on a Shimadzu UV-2550 spectrophotometer. The thermal stability analysis was performed on a TA Instruments Q500 Thermogravimetric analyzer under the nitrogen atmosphere. Each sample (~10 mg) was heated from 25 to 800 °C with a rate of 10 °C min^{-1}. The AFM-IR image was collected at 1711 cm^{-1} on Bruker NanoIR3 instrument. The digital images of the samples were captured by a Canon SX40 HS camera in macro mode. Dynamic mechanical analysis (DMA) of NCB-PUUs was performed on a DMA$^+$450 (01dB-Metravib, Inc.) using tension film mode with a frequency of 1 Hz and strain amplitude of 1%. The stress-strain curves were measured at room temperature and ~20% relative humidity by using a 410R250 Tension Instrument (TEST RESOURCES INC, USA) with a stretching speed of 50 mm min^{-1}. For tensile measurements, the specimens were cut into dog-bone shapes (width: 2 mm; gauge length: 12 mm). Small-angle X-ray scattering (SAXS) patterns were acquired by beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wavelength was chosen as 0.124 nm (E=10 keV), the sample-to-detector distance was 1565 mm.

Synthesis route of PBA:



Fabrication of NCB-PUU sheets. The freshly obtained NCB-PUU (8 g) was dissolved in ethanol (40 ml) in a beaker (100 ml) under stirring. The ethanol solution of NCB-PUU was poured onto a glass slide and evaporated under room temperature for 24 h to remove the ethanol. In this way, NCB-PUU sheet was obtained.

Healing and recycling of NCB-PUU sheets. Healing and recycling of NCB-PUU sheets were conducted under ~20% RH at room temperature. Firstly, NCB-PUU sheet with dog-bone shape (2mm*12mm*0.5mm) was cut into two separate pieces by a razor blade. Then the cut ends were dipped into either water/ethanol mixture or ethanol for 2 min. Next, the two separate pieces were brought into contact, followed by drying the sheet at room temperature for different times. For recycling of NCB-PUU, NCB-PUU sheets were cut into small pieces and dissolved in ethanol at room temperature. The ethanol solution of NCB-PUU was then cast onto a clean glass mold. After removal of ethanol at room temperature, recycled NCB-PUU sheet was obtained.

Dip-coating of NCB-PUUs on model cars. The model car was immersed in the NCB-PUU ethanol solution (50 mg ml^{-1}) and kept into the solution for 2 h. Then, the model car was withdrawn from the solution, followed by drying the model car at room temperature. In this way, the model car was deposited with NCB-PUU coating.

Spraying-coating of NCB-PUUs. An Infinity CRplus spray gun (Harder & Steenbeck) with a 0.4 mm nozzle was used to spray NCB-PUU coatings. The pressure of the spray gun was set as 0.24 MPa and the distance between the nozzle and targeted substrate surface was 12 cm. The NCB-PUU solution with organic dyes was manually sprayed onto the substrate with a spray volume of 0.09 mL cm^{-2}. This process can be repeated to tailor the thickness of the resultant coatings.

Adhesion test of NCB-PUU coatings toward solid substrates. The adhesion of the NCB-PUU coating on glass, stainless steel, aluminum and copper substrates was measured by the cross-cut tape test method following ASTM D 3359 specifications. The coatings deposited on the above substrates were cut into small squares (separated by 1 mm) that form grids. Pressure-sensitive 3M Scotch™ tape was then placed over the grid. After 90s, the tape was removed rapidly. Adhesion strength was expressed with a rating system of 1–5 B, in which 5B means no peeling of film. The optical microscope images shown in Fig. S7 display that no obvious detachment of the cut coatings occurs after the test. This result indicates that NCB-PUU has a 5B adhesion on these substrates.

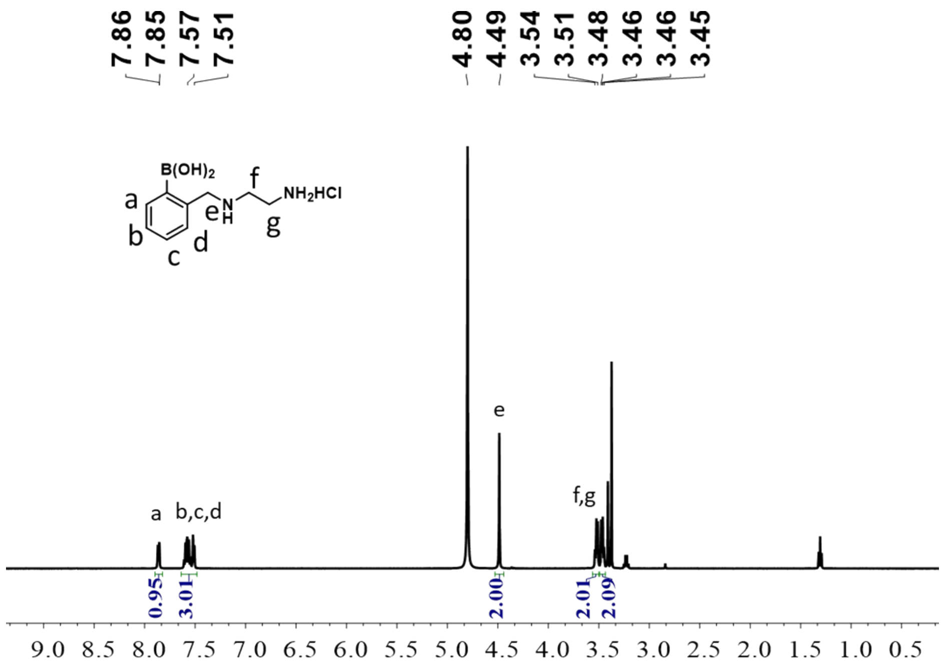


Fig. S1 ^{1}H NMR spectrum of PBA.

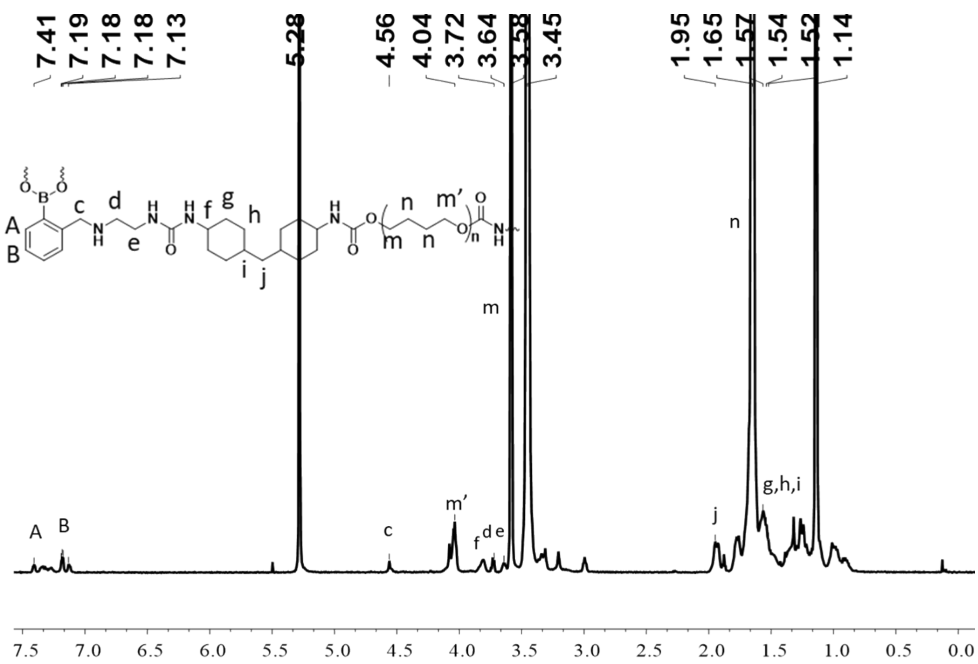


Fig. S2 ^{1}H NMR spectrum of PBA-PUUs.

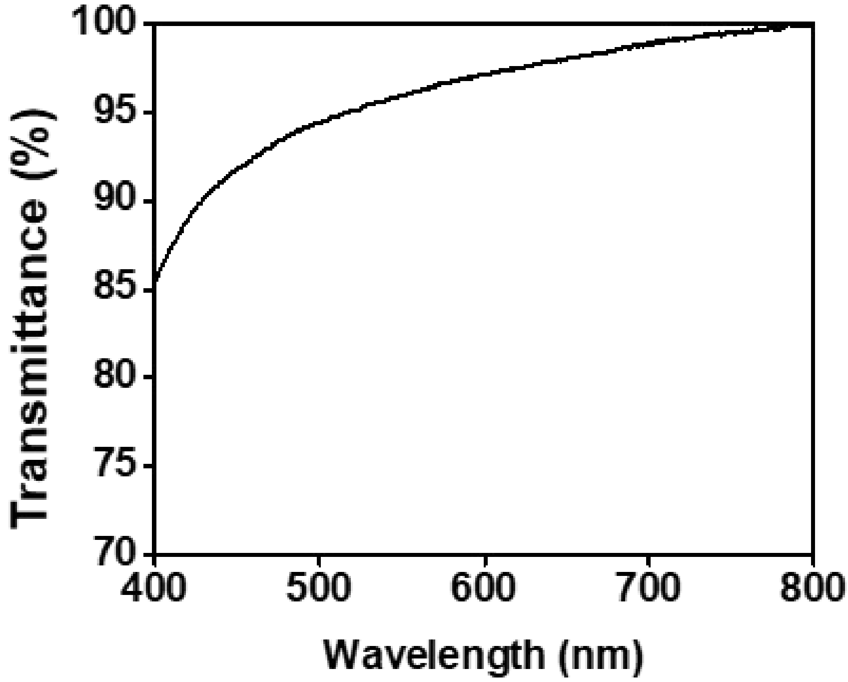


Fig. S3 UV-vis transmission spectrum of NCB-PUU coatings without underlying substrate.

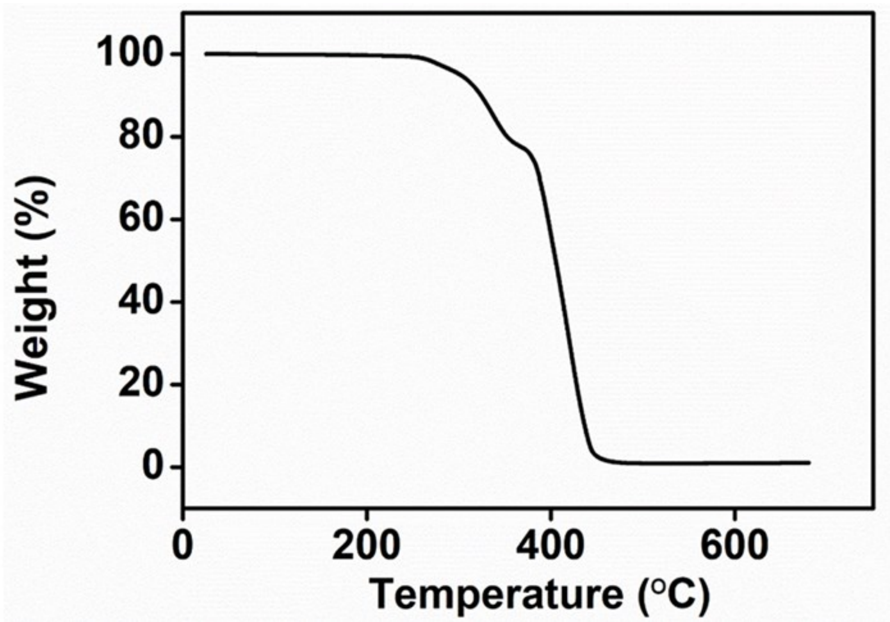


Fig. S4 TGA curve of NCB-PUUs.

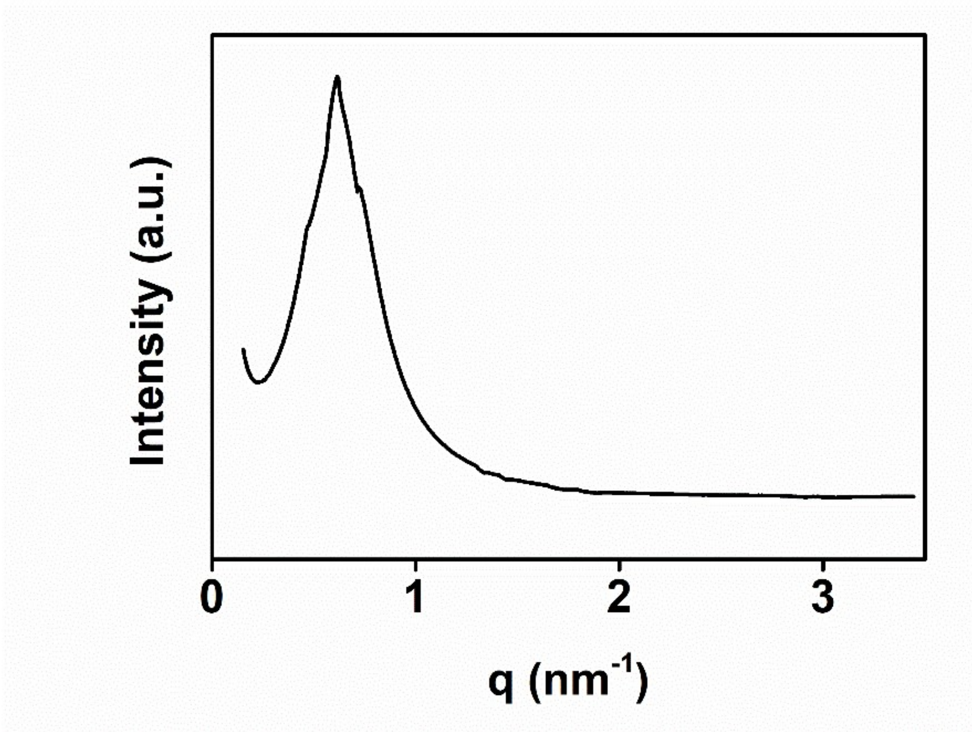


Fig. S5 Small-angle X-ray scattering (SAXS) curve of NCB-PUUs.

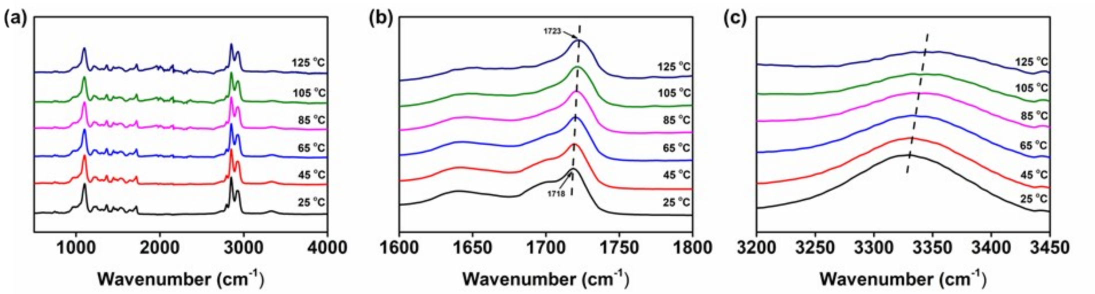


Fig. S6 Variable temperature FT-IR spectra of NCB-PUU in the ranges of 500-4000 cm^{-1} (a), 1600-1800 cm^{-1} (b), and 3200-3450 cm^{-1} (c).

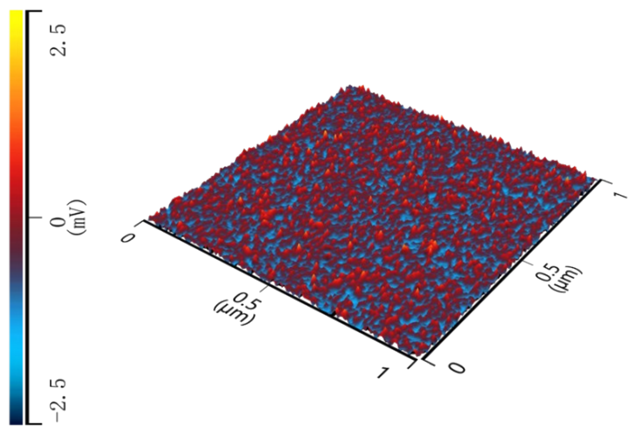


Fig. S7 AFM-IR chemical image shows the distribution of the C=O groups in the separated microphases (red). The AFM-IR image was collected at 1711 cm^{-1}.

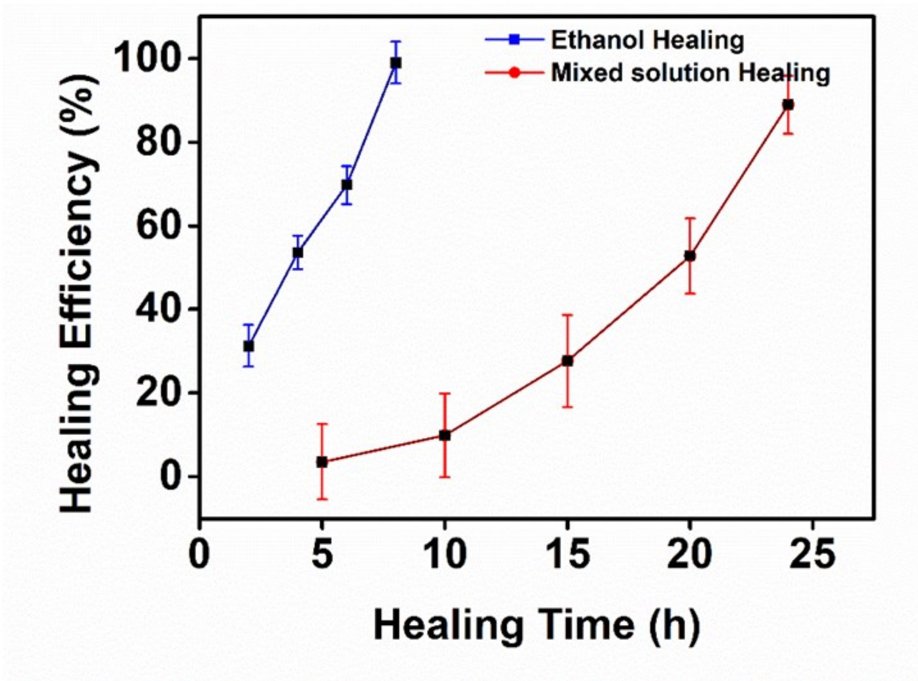


Fig. S8 Comparison of the healing efficiency and healing time of NCB-PUU sheets with the assistance of ethanol and water/ethanol mixture (volume ratio 2:1).

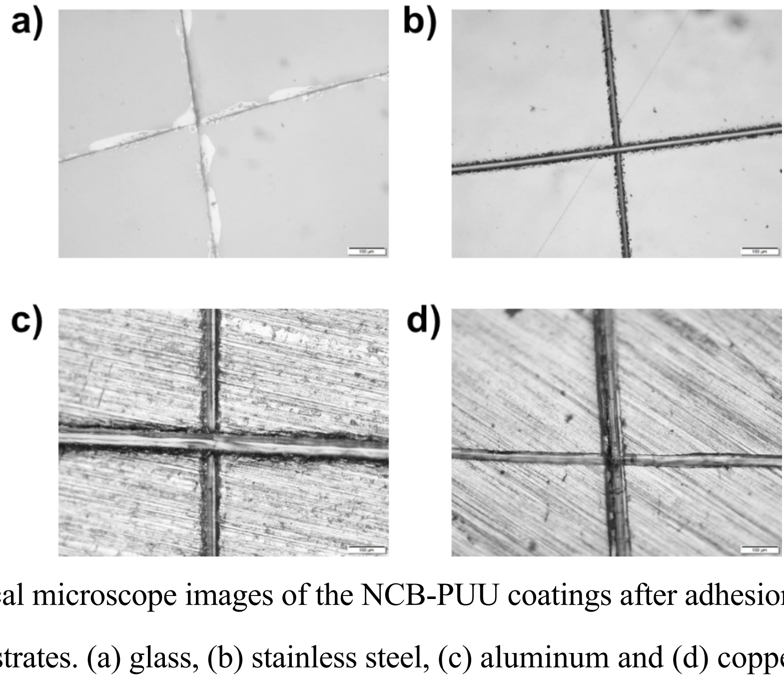


Fig. S9 Optical microscope images of the NCB-PUU coatings after adhesion test on different substrates. (a) glass, (b) stainless steel, (c) aluminum and (d) copper.

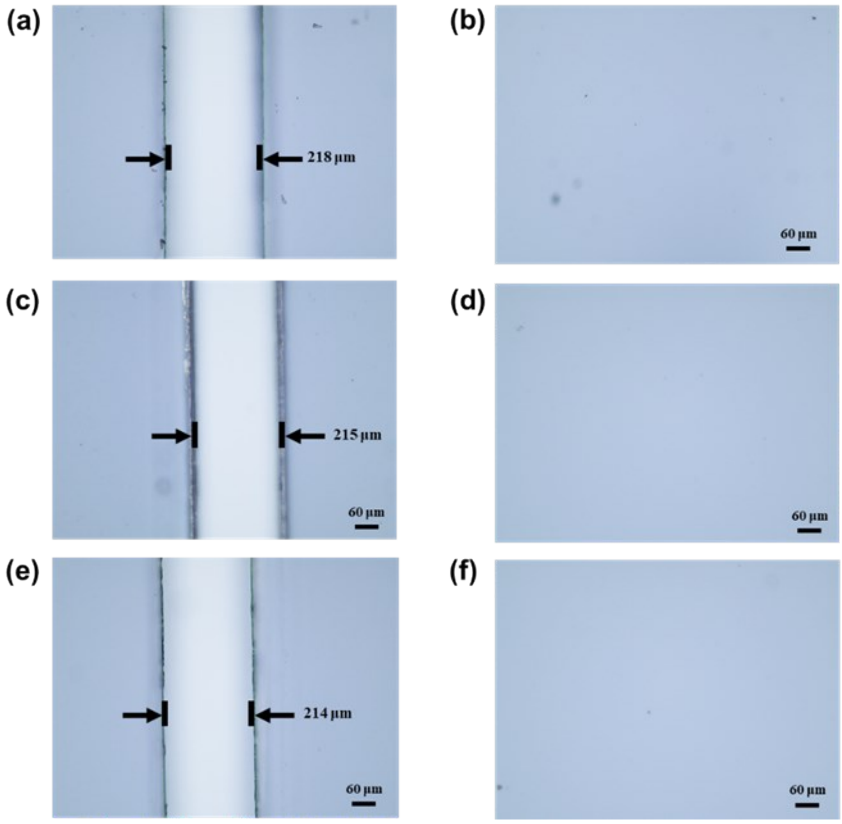


Fig. S10 Optical microscope images of the NCB-PUU sheet during three cycles of cutting/healing process.

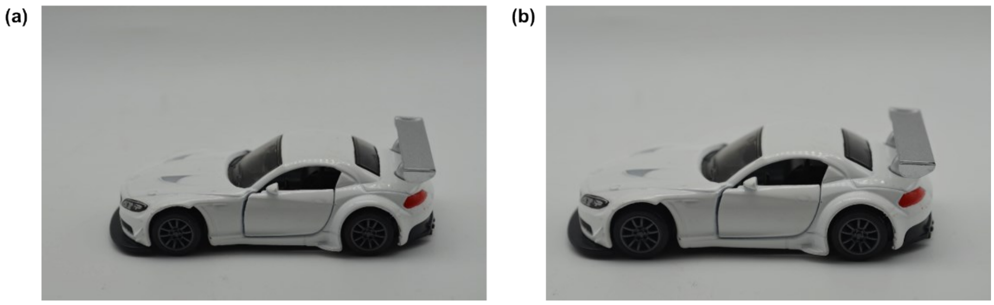


Fig. S11 Digital image of the model car (a) and after pulling out from the solution with homogeneous NCB-PUU coating (b).

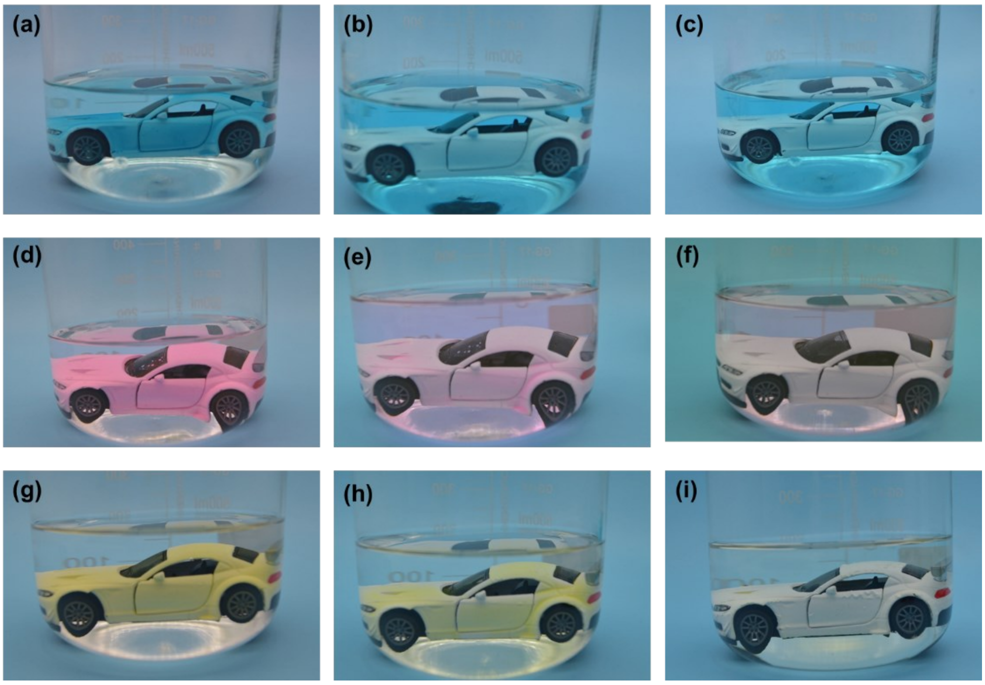


Fig. S12 Digital images of the model car with different colored NCB-PUU coating which was immersed in ethanol for 0 h (a, d, g), 3 h (b, e, h) and 6 h (c, f, i).

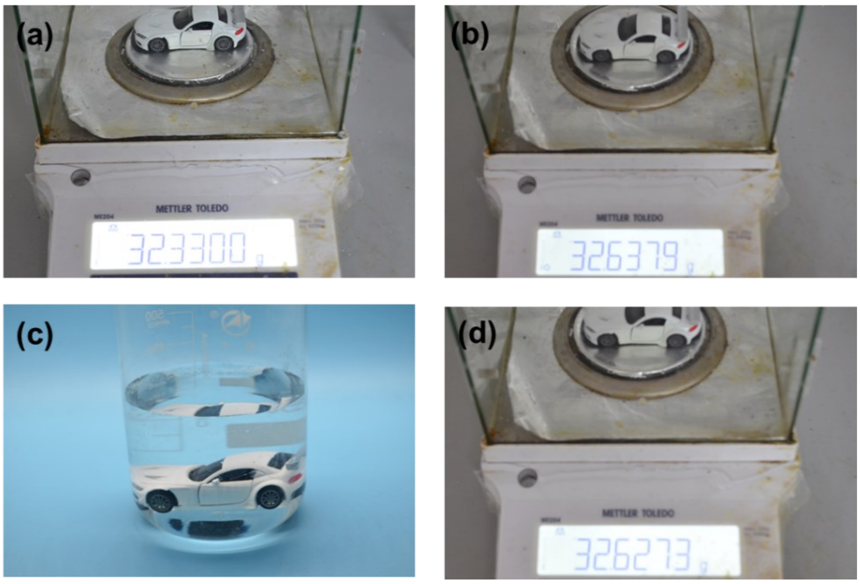


Fig. S13 Mass change of NCB-PUU coating deposited on a model car. (a) As-prepared coating. (b) Immersed in water for 24 h. (c) After immersion in water and being dried.