Electronic Supplementary Information

Regulation of mechanical properties and self-healing performance of polyurethane nanocomposites by tuning the contents of free and associated hydrogen bonds

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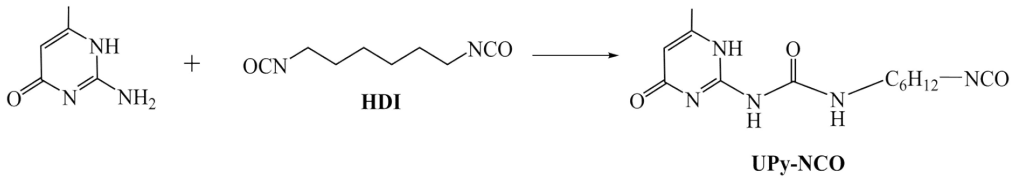
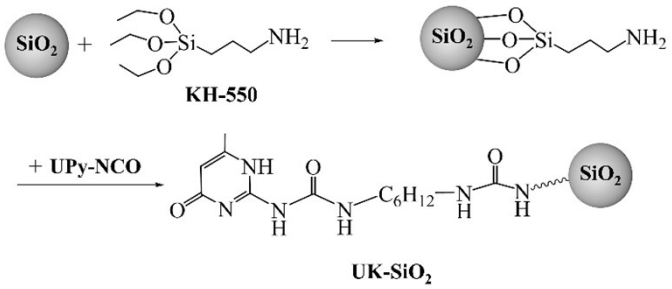
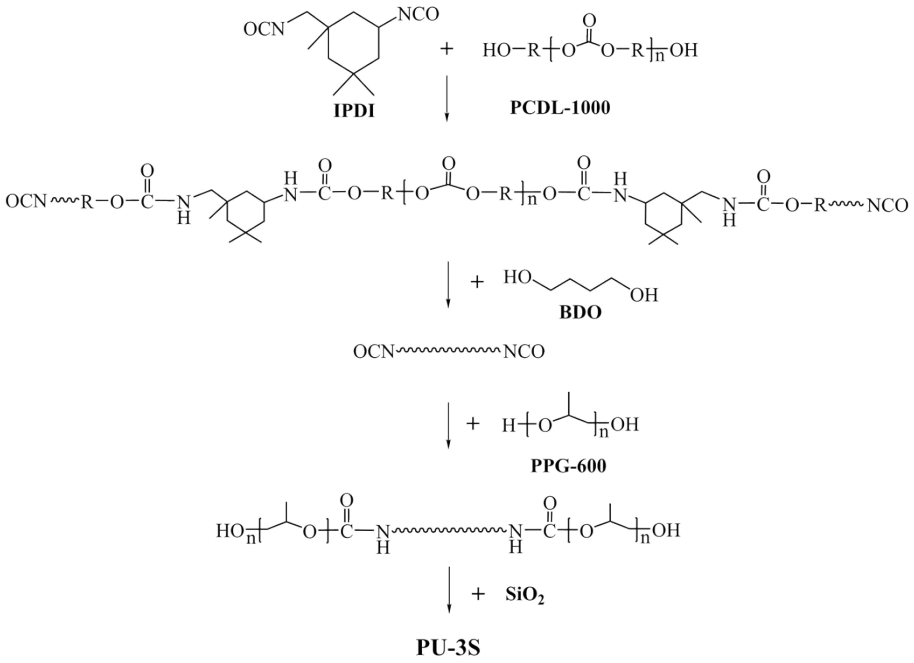


Scheme S1. The synthesis of UPy-NCO.



Scheme S2. The synthesis process of UK-SiO_2.



Scheme S3. The preparation process of PU-3S.

Table S1. Tensile strength of the PU nanocomposites filled with different contents of unmodified SiO_2.

	PU	PU-1S	PU-3S	PU-5S
Tensile strength (MPa)	2.13	2.20	5.89	3.11

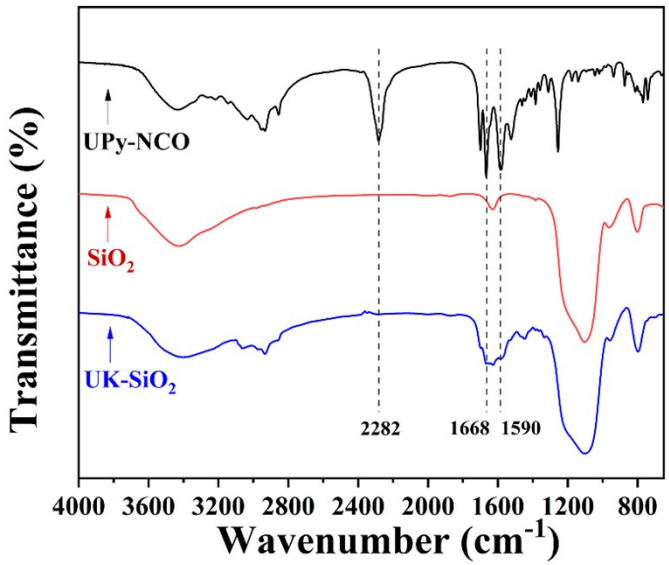


Fig. S1. FTIR spectra of UPy-NCO, unmodified nano-SiO_2 and UK-SiO_2.

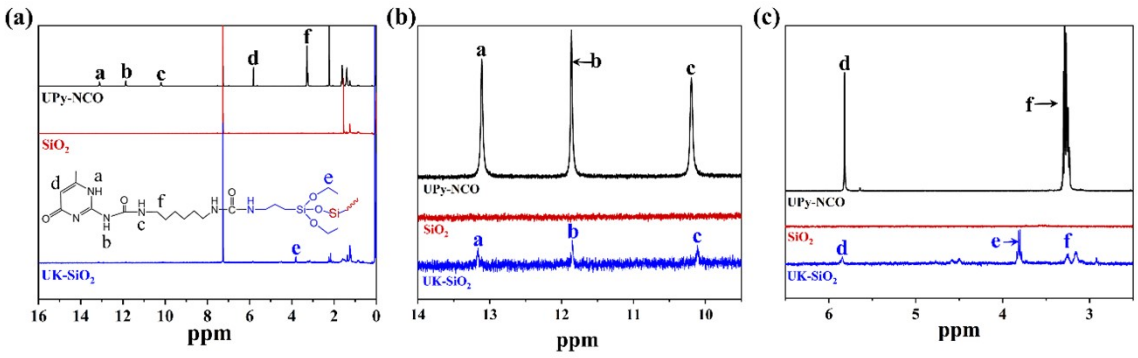


Fig. S2. (a) ^{1}H NMR spectra of UPy-NCO, unmodified nano-SiO_2 and UK-SiO_2; (b, c) locally amplified ^{1}H NMR spectra of UPy-NCO, unmodified nano-SiO_2 and UK-SiO_2.

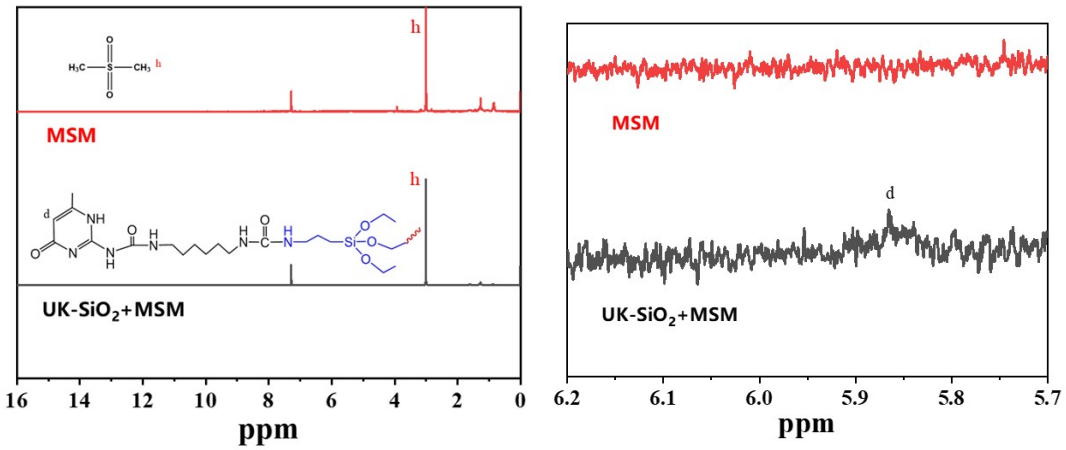


Fig. S3. ^{1}H NMR spectra of UK-SiO_2 particles containing MSM as internal standard (the left panel); locally amplified ^{1}H NMR spectra of UK-SiO_2 particles containing MSM as internal standard (the right panel).

Table S2. Particle size of nano-SiO_2 before and after modification.

	Unmodified nano-SiO_2	UK-SiO_2
Particle size (nm)	114.1	286.4

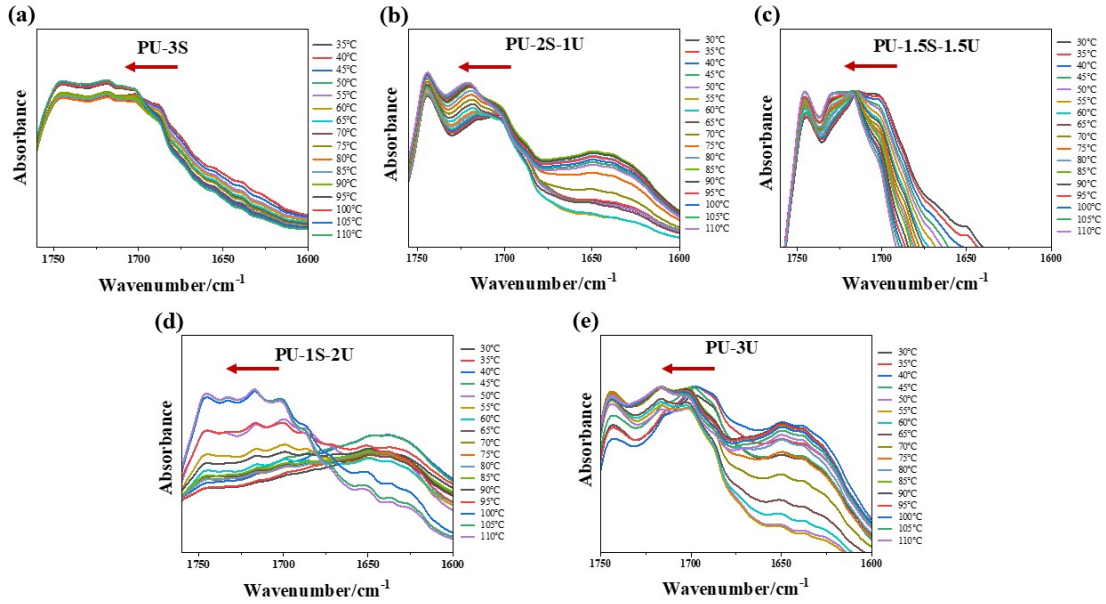


Fig. S4. FTIR spectra of the five filled PU samples, that is, (a) PU-3S, (b) PU-2S-1U, (c) PU-1.5S-1.5U, (d) PU-1S-2U and (e) PU-3U at different temperatures.

Fig. S5. (a) Photo of water contact angle of nano-SiO_2; (b) photo of water contact angle of UK-SiO_2; (c) photo of water contact angle of PU.

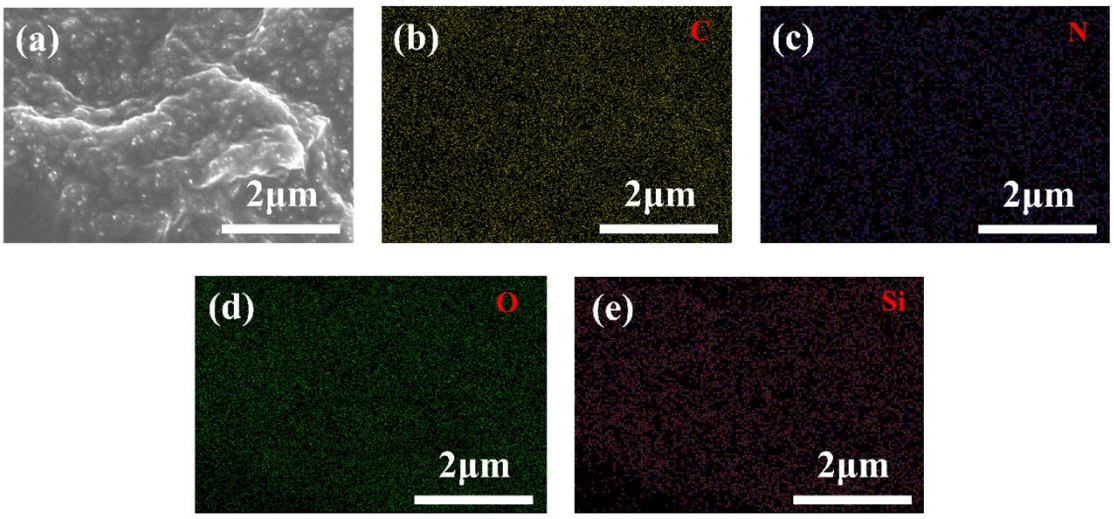


Fig. S6. (a) SEM image of PU-3S; distribution of (b) C element, (c) N element, (d) O element, (e) Si element in PU-3S. The content of C element in PU-3S is the highest, followed by that of O element, Si element and N element. The presence of Si element further indicates that nano-SiO_2 is successfully modified.

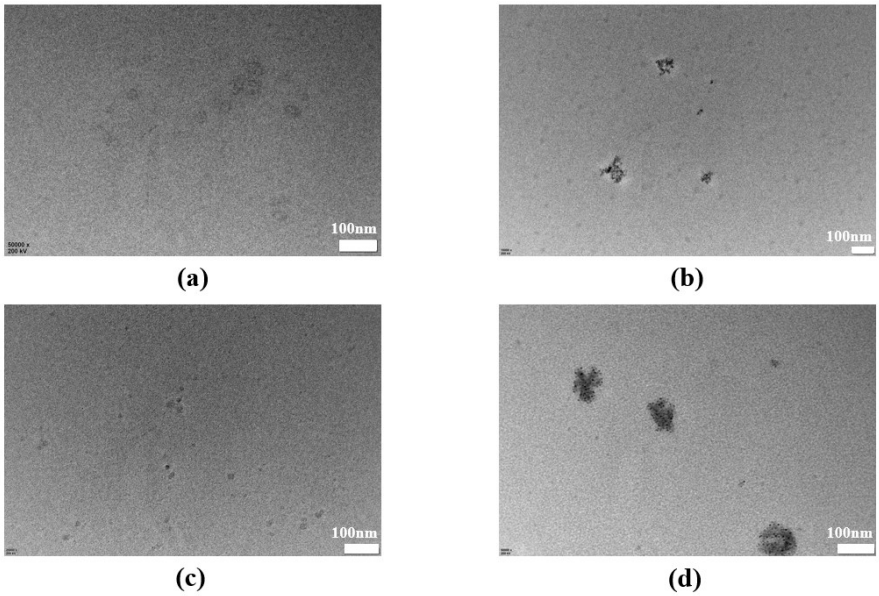


Fig. S7. TEM micrographs of (a) the PU-3S sample, (b) the PU-2S-1U sample, (c) the PU-1S-2U sample and (d) the PU-3U sample, respectively.

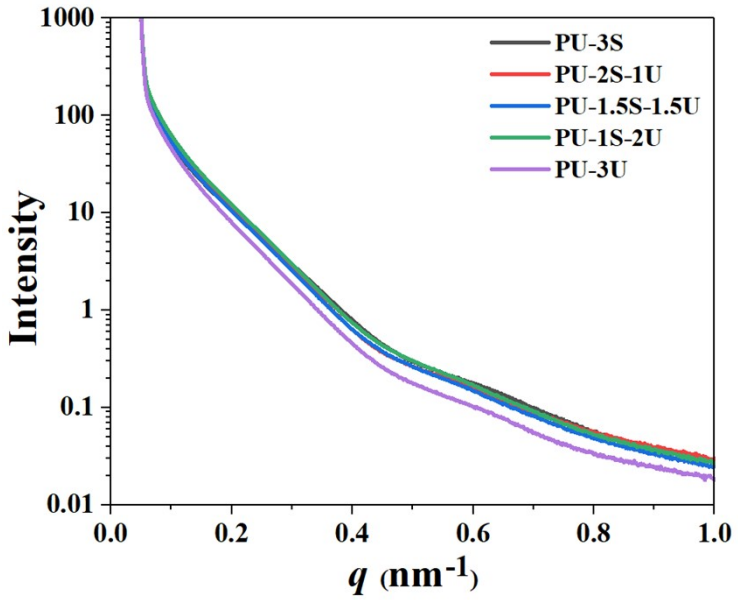


Fig. S8. SAXS curves of the five different PU samples (the PU-3S, the PU-1S-2U, the PU-1.5S-1.5U, the PU-2S-1U and the PU-3U samples).

Table S3. Tensile strengths of the five PU nanocomposites.

	PU-3S	PU-2S-1U	PU-1.5S-1.5U	PU-1S-2U	PU-3U
Tensile strength (MPa)	5.89	18.94	6.8	5.24	13.09

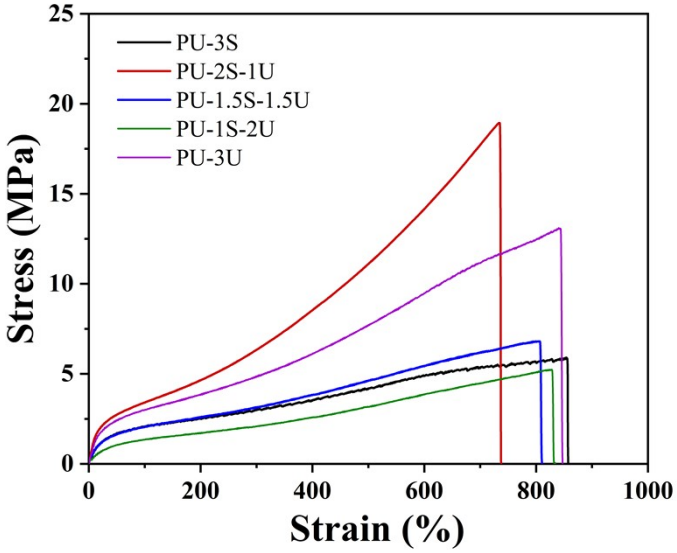


Fig. S9. Stress-strain curves of the different self-healing PU samples.

Table S4. The healing efficiency of the five PU nanocomposites under different self-healing conditions.

	25℃-1h	25℃-2h	25℃-3h	45℃-1h	60℃-1h
PU-3S	55.35%	63.84%	71.14%	87.60%	92.19%
PU-2S-1U	24.39%	35.27%	58.13%	77.45%	93.98%
PU-1.5S-1.5U	54.41%	63.38%	73.68%	90.44%	**107.94%**
PU-1S-2U	58.59%	63.93%	76.53%	91.60%	**120.23%**
PU-3U	52.94%	61.88%	68.75%	85.10%	97.78%

Table S5. Healing efficiency of the five PU nanocomposite samples with different thickness healed at 25℃ for 3 h.

	0.5 mm	1 mm	1.5 mm	2 mm
PU-3S	68.46%	71.14%	73.24%	74.07%
PU-2S-1U	55.91%	58.13%	59.23%	61.85%
PU-1.5S-1.5U	70.17%	73.68%	74.83%	75.39%
PU-1S-2U	74.04%	76.53%	77.61%	78.43%
PU-3U	63.41%	68.75%	70.48%	71.32%

Table S6. Tensile strengths of the five PU nanocomposite samples with different thickness.

	PU-3S	PU-2S-1U	PU-1.5S-1.5U	PU-1S-2U	PU-3U
Tensile strength (MPa)-0.5 mm	5.43	16.72	5.64	5.04	11.34
Tensile strength (MPa)-1 mm	5.89	18.94	6.80	5.24	13.09
Tensile strength (MPa)-1.5 mm	6.76	19.56	7.32	5.69	14.3
Tensile strength (MPa)-2 mm	7.05	20.21	8.10	6.51	15.2

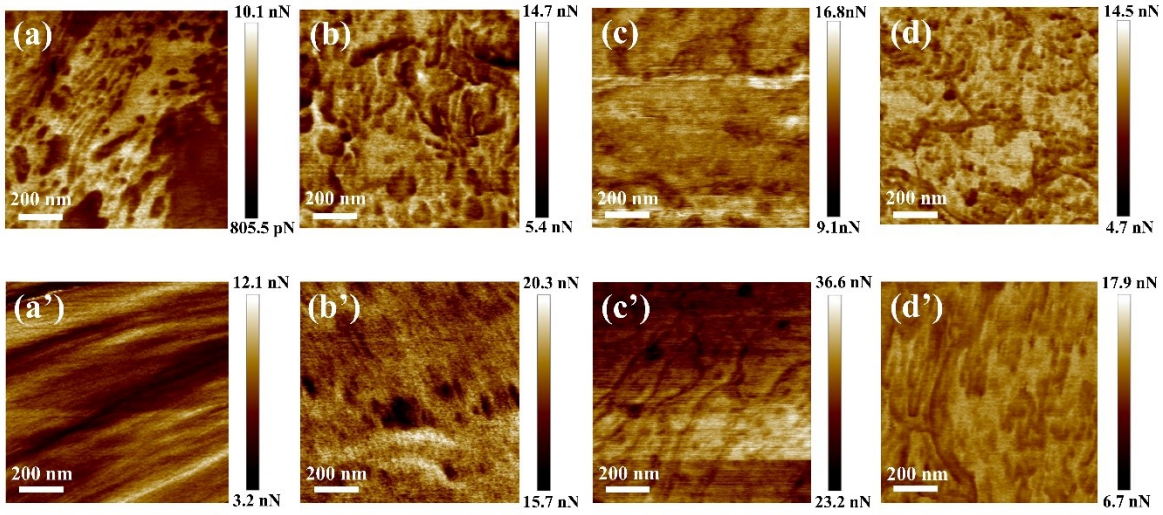


Fig. S10. (a~d) are the AFM adhesion distribution diagrams of PU-2S-1U, PU-3S, PU-1S-2U and PU-3U surfaces, respectively; (a'~d') are the AFM adhesion distribution diagrams of PU-2S-1U, PU-3S, PU-1S-2U and PU-3U cross-sections, respectively.