Self-healing nanocomposites *via* N-doped GO promoted "click chemistry"

V. Siva Prasanna Sanka,[a]† Sravendra Rana,[b]†* Poonam Singh,[b] Abhishek K. Mishra, [b] Pankaj Kumar,[b] Manjeet Singh,[c] Nanda Gopal Sahoo,[d] Wolfgang H. Binder,[e]* Gun Jin Yun,[f]* Chanwook Park[g]*

[a]*Department of Mechanical Engineering, University Institute of Engineering, Chandigarh University, Mohali, India*

[b]*University of Petroleum & Energy Studies (UPES), School of Engineering, Energy Acres, Bidholi, Dehradun, 248007, India*

[c]*Department of Chemistry, School of Physical Sciences, Mizoram University, Aizawl 796004, Mizoram, India*

[d]*Prof. Rajendra Singh Nanoscience and Nanotechnology Centre, Department of Chemistry, D.S.B. Campus, Kumaun University, Nainital-263001, Uttarakhand, India*

[e]*Chair of Macromolecular Chemistry, Institute of Chemistry, Faculty of Natural Science II, Martin Luther University Halle-Wittenberg, Von-Danckelmann-Platz 4, Halle, 06120, Germany*

[f] *Department of Aerospace Engineering, Seoul National University, Gwanak-gu Gwanak-ro 1, Seoul, 151-744, South Korea*

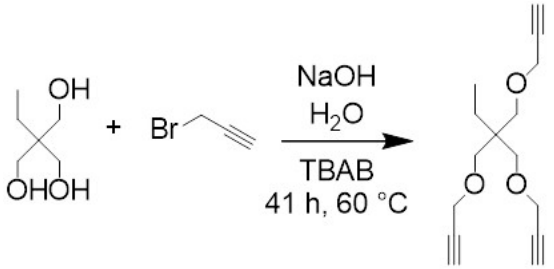
[g] *Department of Mechanical Engineering, Northwestern University, Evanston 60208, IL, USA*

†Authors made equal contribution.

**Correspondence: Email: srana@ddn.upes.ac.in; chanwookpark2024@u.northwestern.edu; gunjin.yun@snu.ac.kr; wolfgang.binder@chemie.uni-halle.de*

Preparation of self-healing agents

Preparation of trivalent alkyne moiety



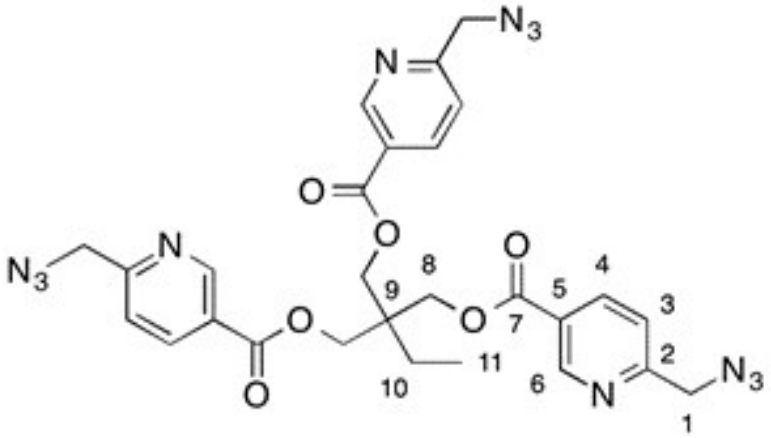
Scheme S1 Synthesis of trimethylolpropane tripropargyl ether (TMPTPE)

The synthesis was carried out under a dry nitrogen atmosphere (Figure 16). A three-necked round bottom flask equipped with a mechanical stirrer, reflux condenser, and rubber septum was heated under vacuum and flushed several times with nitrogen. Trimethylol propane (149.1 mmol, 20.0 g), sodium hydroxide (6.0 eq, 894.4 mmol, 35.8 g) and Tetra-N-Butylammonium Bromide (TBAB) (0.04 eq, 7.0 mmol, 2.4 g) were dissolved in distilled water (4.0 mL). Afterward, propargyl bromide (6.0 eq, 894.4 mmol, 85.4 mL, 134.1 g, 80.0 wt % solution in toluene) was added dropwise over one hour, and then the temperature was increased to 60 ˚C, and the reaction

mixture was heated for 41 h at 60 ˚C. On completion of the reaction (TLC control, $CHCl_3$, R_f = 0.85, blue stain), the reaction mixture was cooled down to room temperature. Thereafter, the solution was diluted with DCM (150.0 mL) and centrifuged (three times, ten ˚C, 5000 rpm, 5 min) to separate the formed salt. The combined organic phases were extracted with distilled water (five times, 500.0 mL) and dried over Na_2SO_4. After filtration, the solvent was removed in a vacuum, and the crude product was purified by column chromatography (SiO_2, 230–400 mesh, Merck (Darmstadt, Germany), to obtain trivalent alkyne as a light-yellow liquid in a yield of 75%.

Preparation of trivalent azide moiety

The procedure opted for the preparation of trivalent azide is taken from the literature (Polymer Chemistry, 2016, 7, 2342), and the structure was confirmed by ^1H and ^{13}C-NMR (Figure 18,19).



Scheme S2 Structure of 2-(((6-(azidomethyl)nictotinoyl)oxy)methyl)-2-2(hydroxymethyl)propane-1,3-diyl bis(6-(azidomethyl)nicotinate)

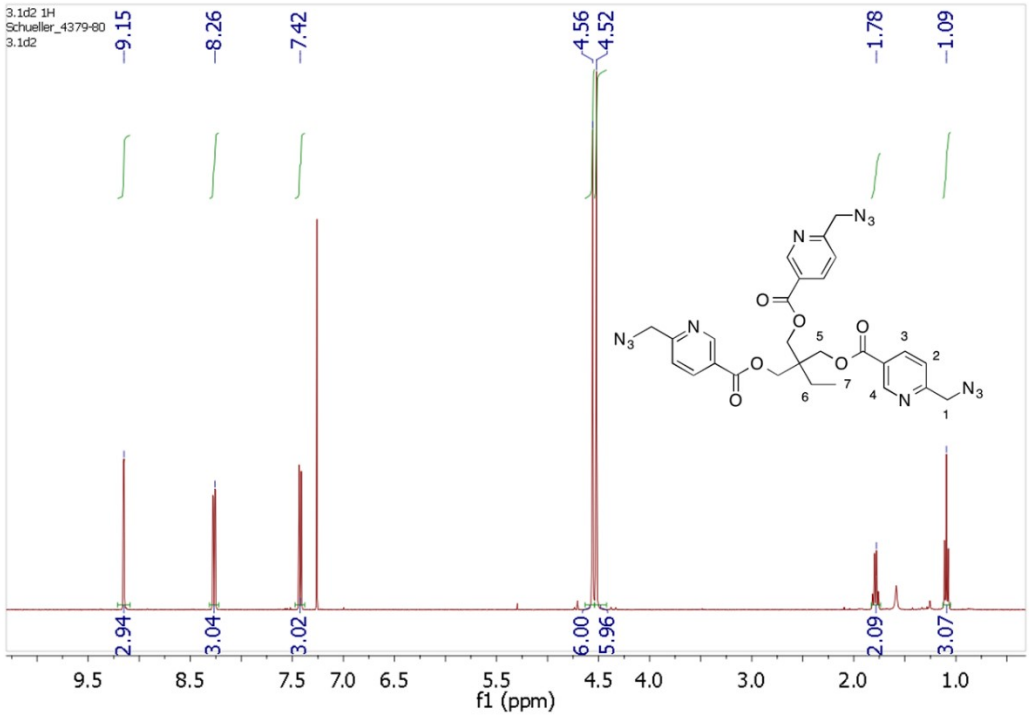


Figure S1. H NMR for 2-(((6-(azidomethyl)nictotinoyl)oxy)methyl)-2-2(hydroxymethyl)propane-1,3-diyl bis(6-(azidomethyl)nicotinate)

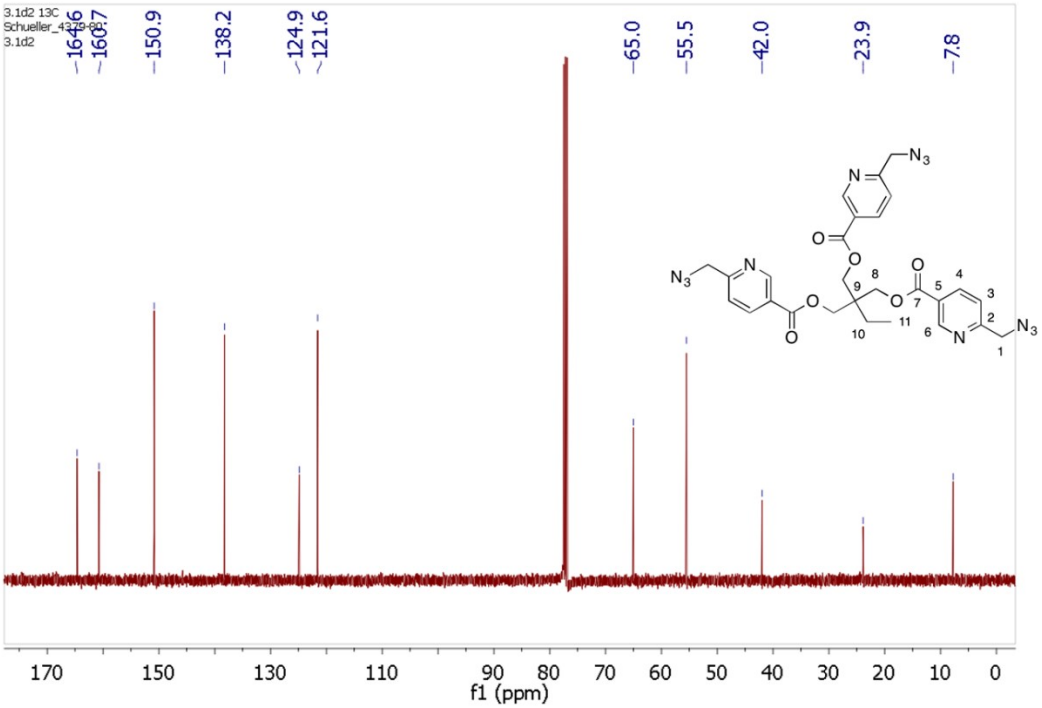


Figure S2. C13 NMR for 2-(((6-(azidomethyl)nictotinoyl)oxy)methyl)-2-2(hydroxymethyl)propane-1,3-diyl bis(6-(azidomethyl)nicotinate)

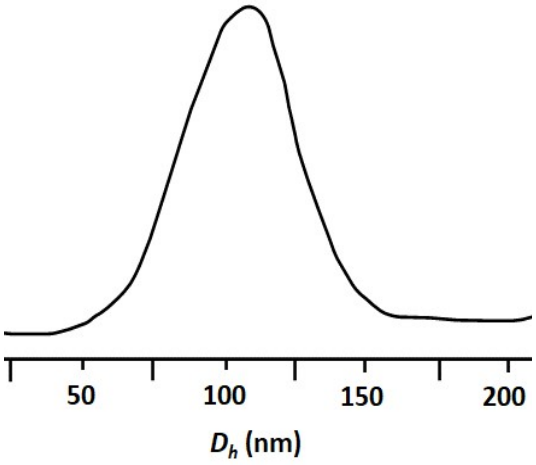


Figure S3. DLS graph of the prepared capsules

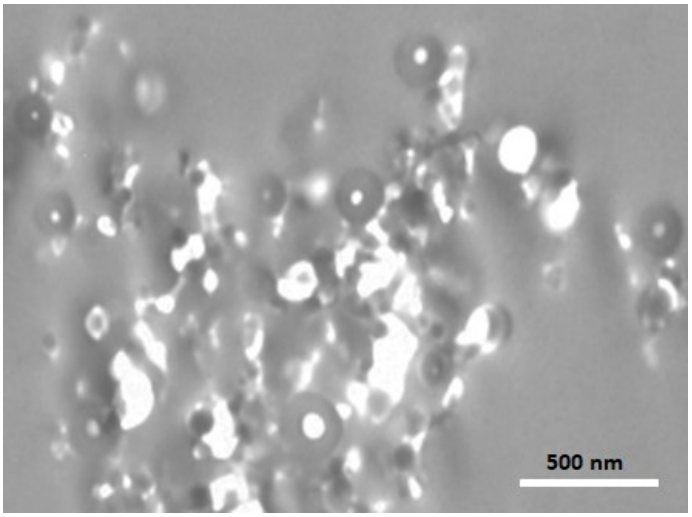


Figure S4. TEM images for the composites consisting of nanocapsules

Molecular Dynamics (MD) simulation details

Table S1 Atomic composition of TRGO and NRGO

Element	TRGO		NRGO	
	Ref [1] Atomic %	MD # of atoms	Ref [1] Atomic %	MD # of atoms
C	91.06	103	85.93	95
H	1.18	30	0.93	30
N	-	-	9.28	10
O	7.76	7	3.86	4
Atomic mass (g/mol)		1379.37		1375.35

Table S2 Molecular composition of epoxy, epoxy + TRGO and epoxy +NRGO nanocomposites.

Component	Epoxy	Epoxy + TRGO	Epoxy + NRGO
DGEBA	250	250	250
DETA	100	100	100
Nanofiller	-	3	3
Number of atoms	14,250	14,670	14,667
Filler weight percentage (%)	-	4.16	4.15

General settings for MD simulations are listed as follows:

1. The polymer consistent force field (PCFF) is adopted to calculate inter-and intermolecular dynamics [2].
2. Geometry optimization is the first step when an MD model starts to run in LAMMPS. We use 10^{-4} (unitless). Furthermore, 0.5 (Kcal/mol $\cdot$ Å) stopping tolerance for energy and force, respectively.
3. Atomic cutoff of 11.5 Å for non-bonded interactions.
4. Ewald summation method with 10^{-4} accuracy (desired relative error in forces).
5. Periodic boundary conditions in all cartesian directions.

The pure epoxy model is built by mixing 250 DGEBA molecules with 100 DETA molecules. To crosslink the epoxy resin, dynamic crosslink simulations are conducted in LAMMPS, using the 'fix bond/create' function. The procedure is summarized here:

1. Geometry optimization for initial model
2. NVT ensemble dynamics at 600K for 1ns with a timestep of 0.5 fs.
3. NPT ensemble dynamics from 600K to 400K at atmospheric pressure for 1ns with a timestep of 1 fs.
4. Connect reactive atoms of DGEBA (carbons on epoxide groups) and DETA (nitrogen) using 'fix bond/create' command.
5. Repeat step 4 until the crosslink density hits 80%. Note that the temperature is set at 400K.
6. Crosslinked model is then cooled down to 300K for 1ns of NPT ensemble dynamics.

Both epoxy + TRGO and NRGO nanocomposites are generated by adding three graphene oxide flakes to the previous epoxy model and going through the same dynamic crosslink simulations described above.

Mechanical tensile tests are performed on equilibrated models. We followed the protocol for uniaxial tensile tests reported in [3]. A uniaxial strain rate of $2 \times 10^8/s$ is used and the tensile test is performed until the engineering strain reaches 0.06.

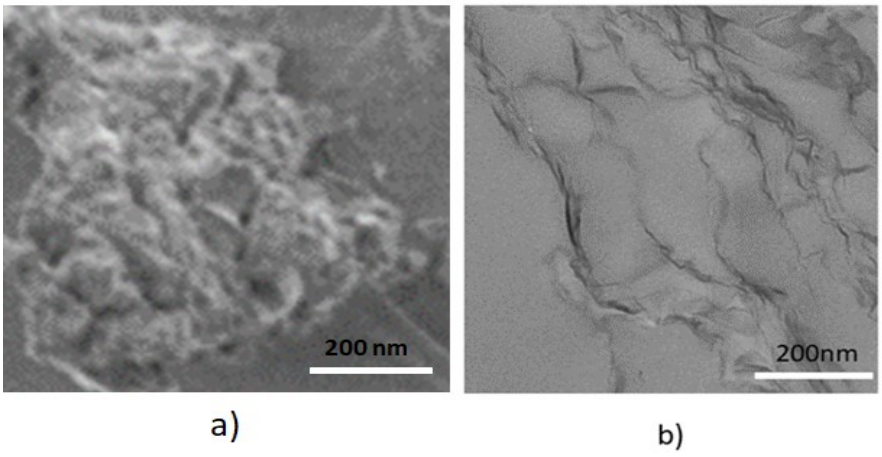


Figure S5. TEM images of a) homogenous (Cu(PPh3)3 F) and b)heterogeneous catalyst NRGO/Cu(I) dispersion in the epoxy matrix.

References

1. Sanka, R.S.P., et al., *Nitrogen-doped graphene stabilized copper nanoparticles for Huisgen [3+ 2] cycloaddition "click" chemistry.* Chemical Communications, 2019. **55**(44): p. 6249-6252.
2. Sun, H., et al., *An ab initio CFF93 all-atom force field for polycarbonates.* Journal of the American Chemical Society, 1994. **116**(7): p. 2978-2987.
3. *C. Park, J. Jung and G. J. Yun, Thermomechanical properties of mineralized nitrogen-doped carbon nanotube/polymer nanocomposites by molecular dynamics simulations, Compos. Part B Eng., 2019, 161, 639–650.*