

A novel method to introduce acidic and basic bi-functional sites in the graphitic carbon nitride for sustainable catalysis: Cycloaddition, esterification, and transesterification reactions

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Electronic Supporting Information

Table S1. Comparison of the catalytic activity in the cycloaddition reaction of CO₂ to epichlorohydrin over some selected MOF, zeolite, amine functionalized silica, metal complex catalysts reported in literature.

Catalyst	ECH (mM)	Solvent	Catalyst amount (mg)	CO ₂ press. (Bar)	Temp. (°C)	Time (h)	Conv. (%)	Select. (%)	Ref.
Zeolite beta	18	CH ₃ CN (10 mL)	150	6.9	120	3	99.6	93.9	[1]
MCM-41-Imi/Br	30	None	300	25	90	4	100	97.0	[2]
MOF, Cu ₃ (BTC) ₃	18	None	100	7	100	4	63.8	51.8	[3]
Fe(III) complex (TBAB-co-catalyst)	70	None	24.6 mg (1.75×10 ⁵ mol)	20	100	6	78	Not indicated	[4]
Zn-SBA-15/KI	34.5	None	50	10	80	8	99.0	99.0	[5]
MOF, ZIF-8	18	None	100	7	100	4	98.2	33.4	[6]
Adenine-modified Ti-SBA-15	18	None	100	6.9	120	3	93.9	89.1	[7]
S-CN(UTU)-60	63	None	50	10	100	4	92.8	99.0	This work

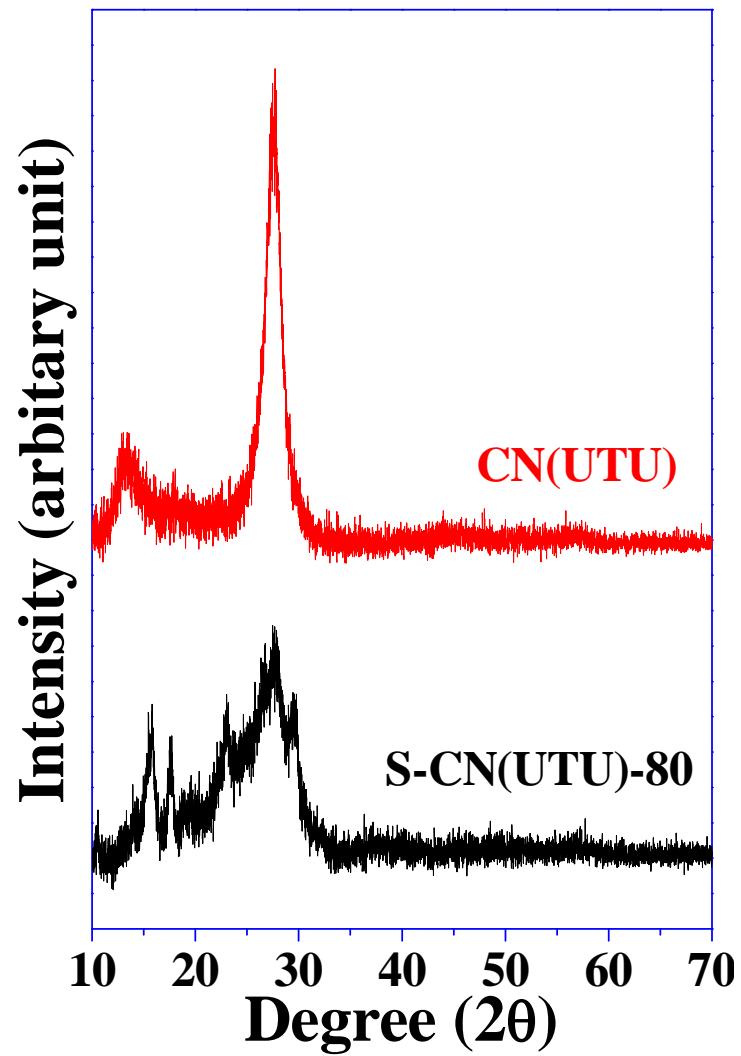


Figure S1. XRD patterns of CN(UTU) and 80% aqueous H_2SO_4 treated sample S-CN(UTU)-80.

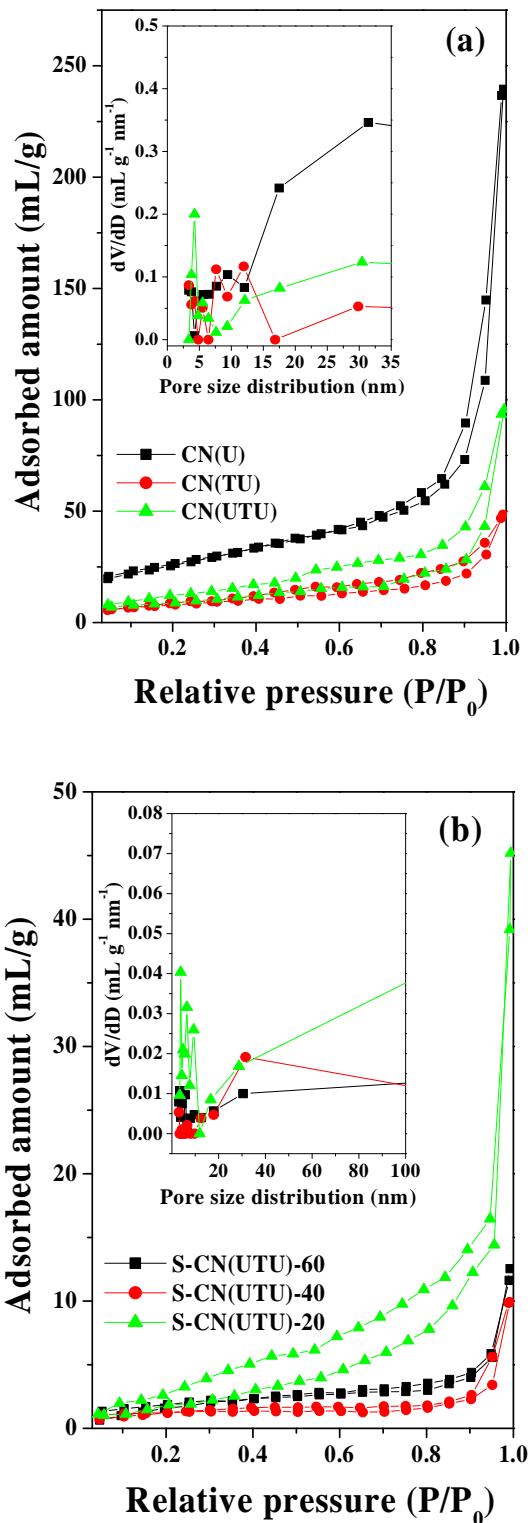


Figure S2. N_2 adsorption-desorption isotherms of (a) carbon nitrides prepared from urea, thiourea and urea-thiourea, (b) aqueous H_2SO_4 treated CN(UTU) materials. Inset shows the pore size distribution.

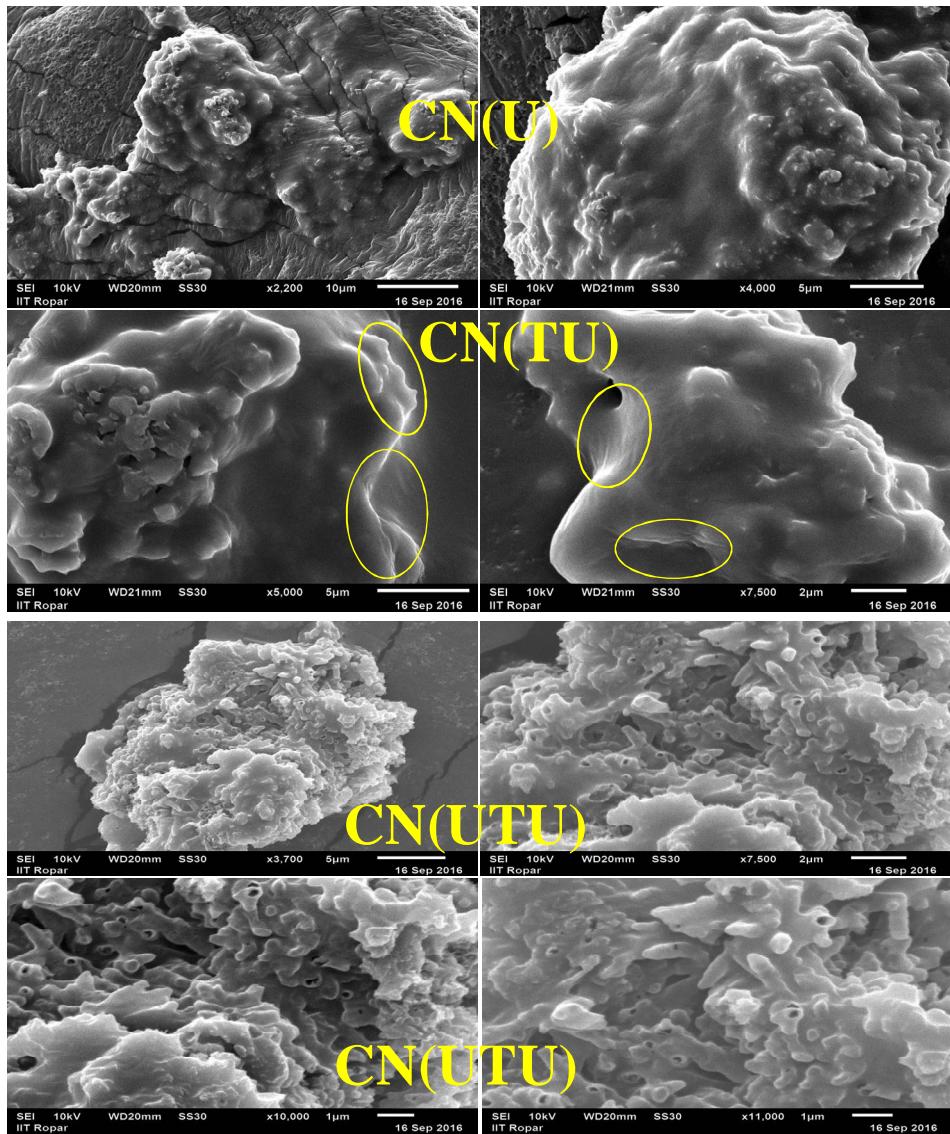


Figure S3. SEM images of carbon nitrides prepared using different precursors.

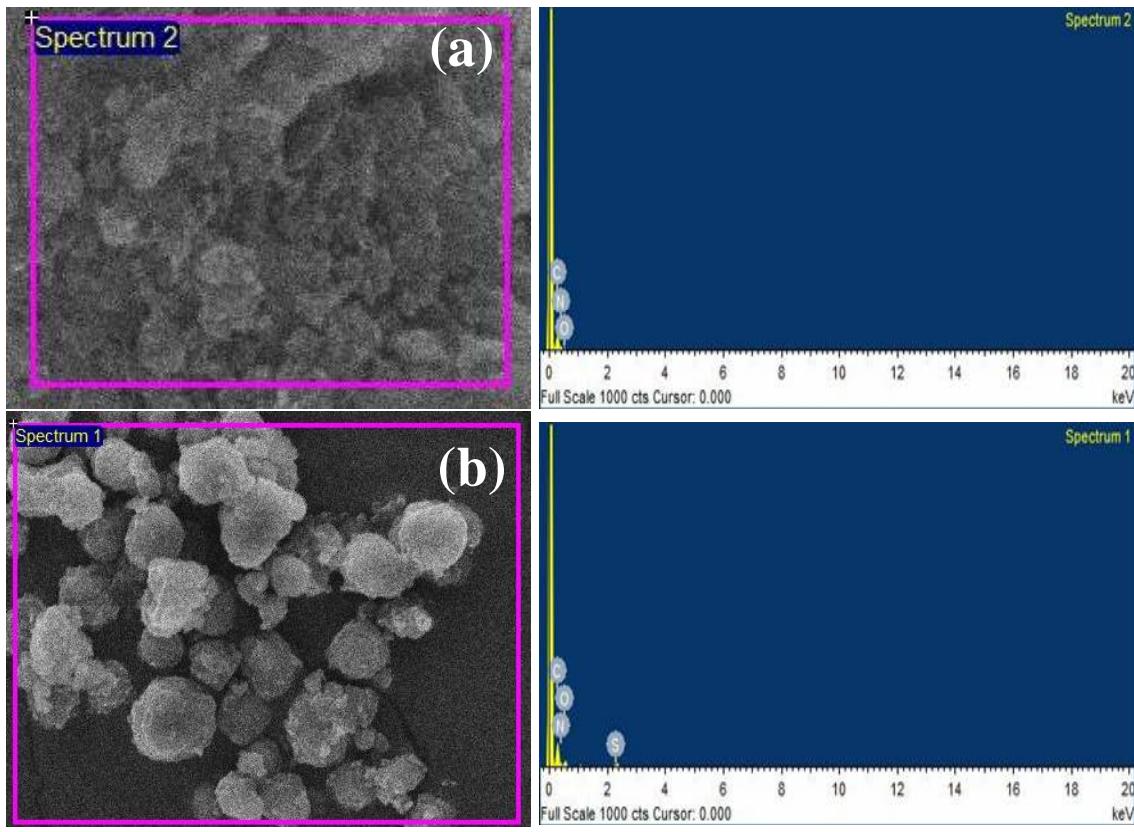


Figure S4. SEM image (left panel) and corresponding EDAX spectra (right panel) for (a) CN(UTU) and (b) S-CN(UTU)-60.

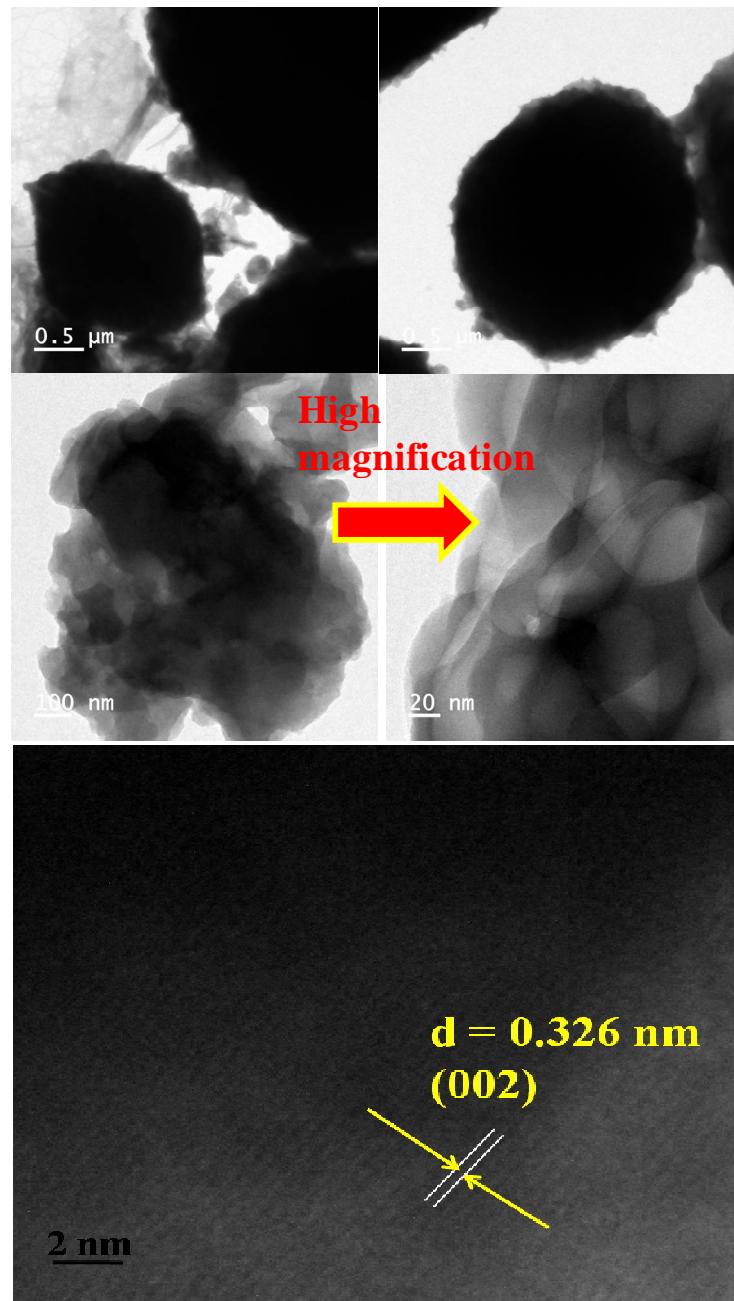


Figure S5. TEM and HRTEM images of S-CN(UTU)-60 in different magnifications.

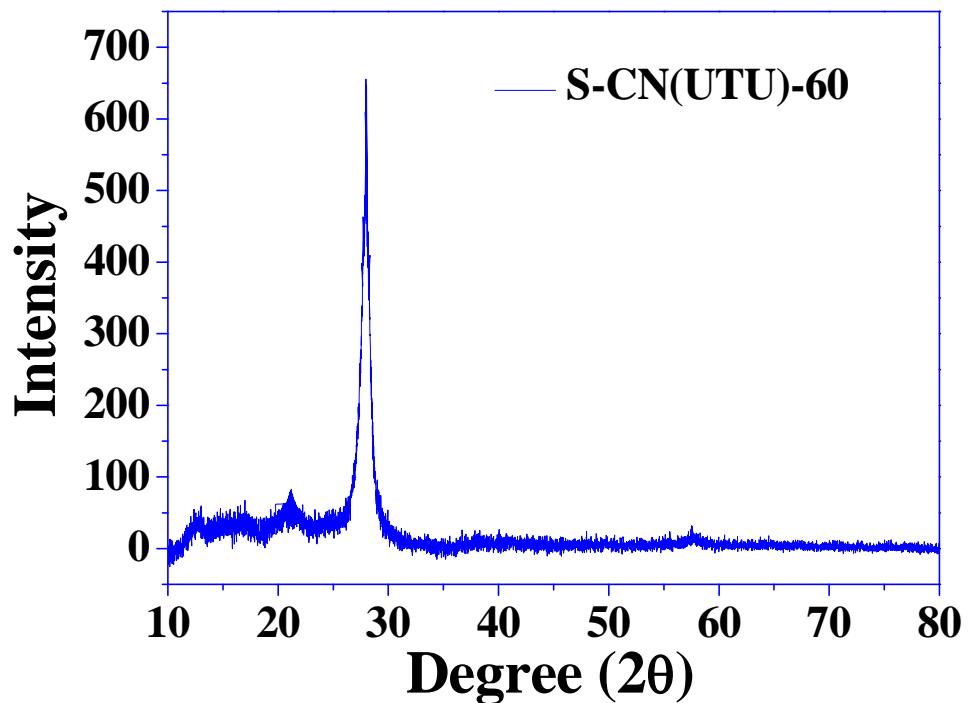


Figure S6. XRD pattern of S-CN(UTU)-60 after 5th recycle.

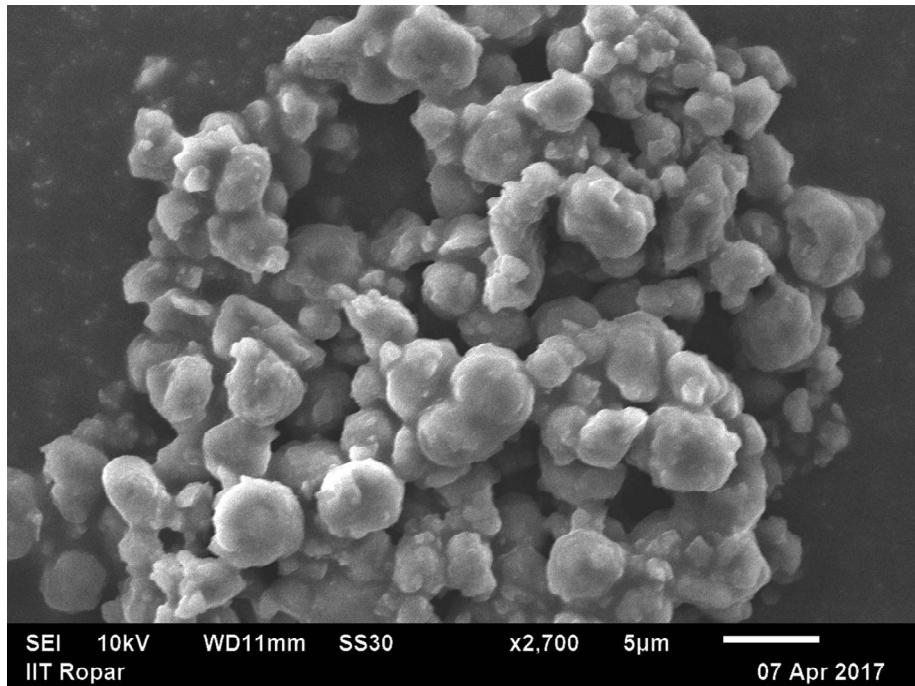


Figure S7. SEM image of S-CN(UTU)-60 after 5th recycle.

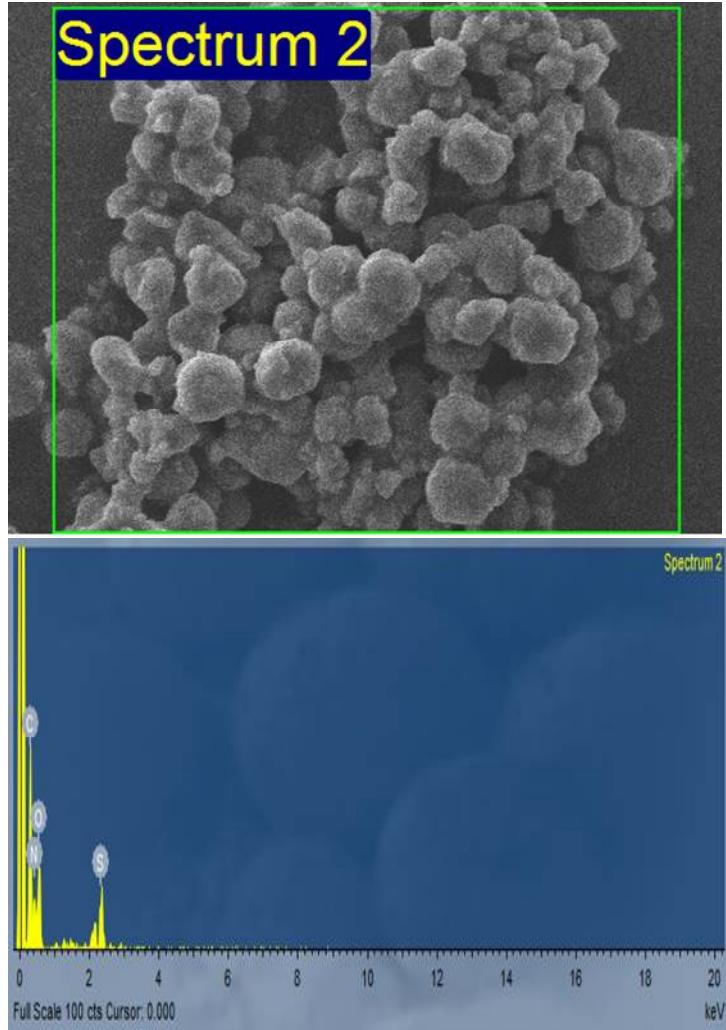


Figure S8. SEM image and corresponding EDAX analysis of the catalyst S-CN(UTU)-60 after 5th recycle.

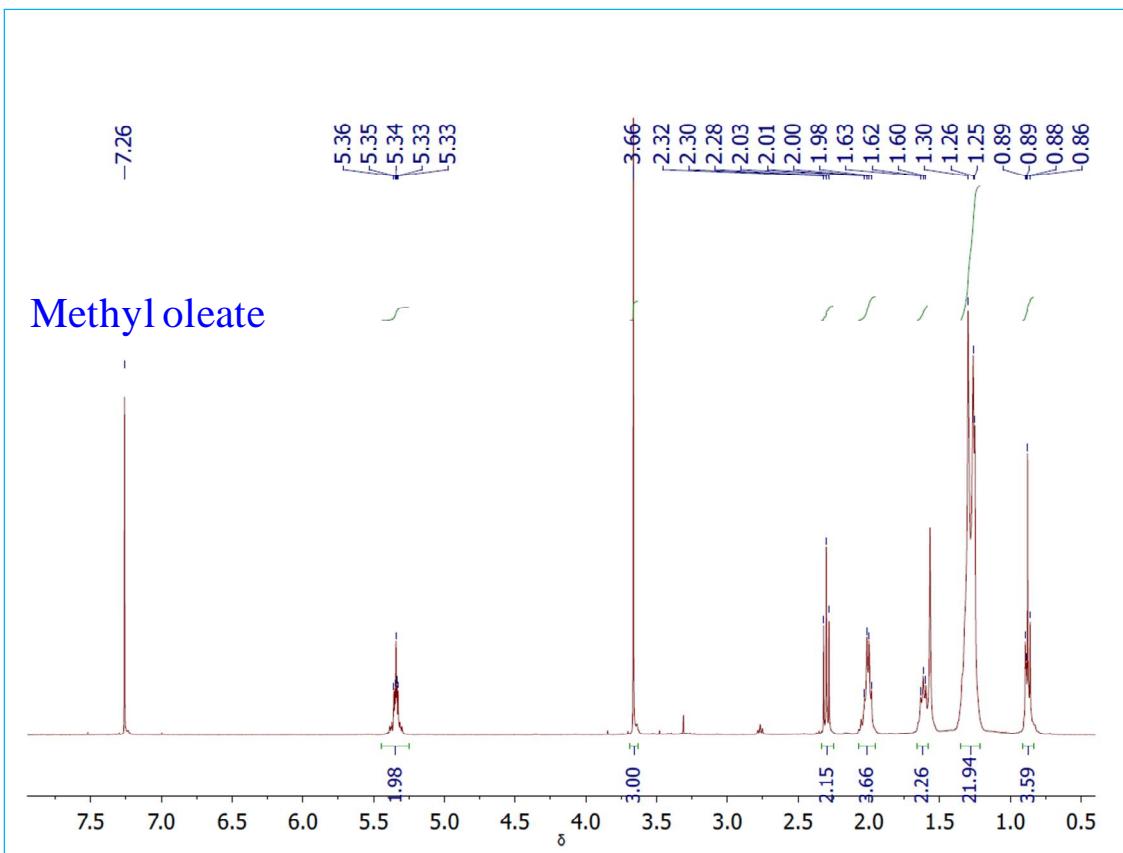
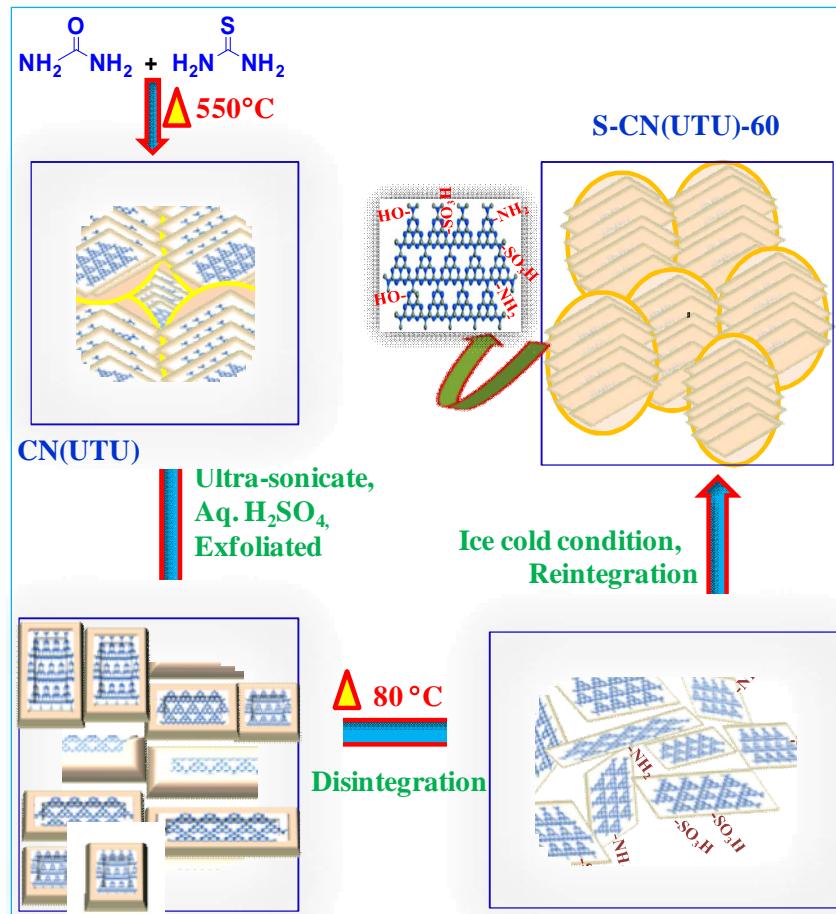
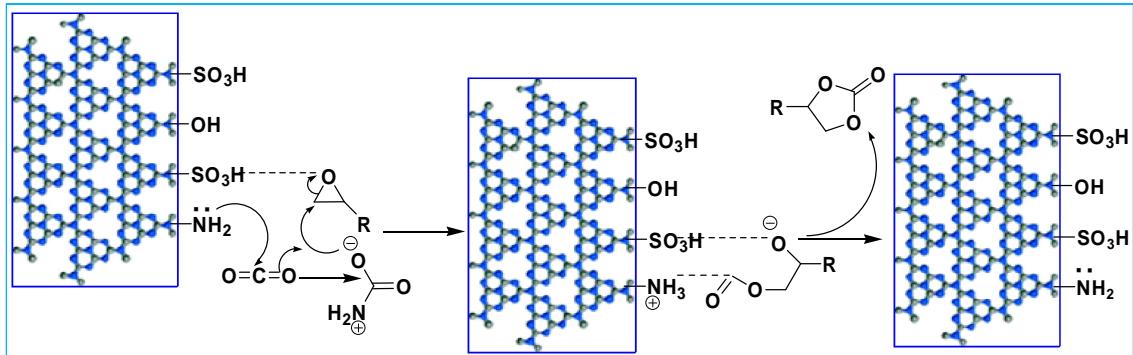


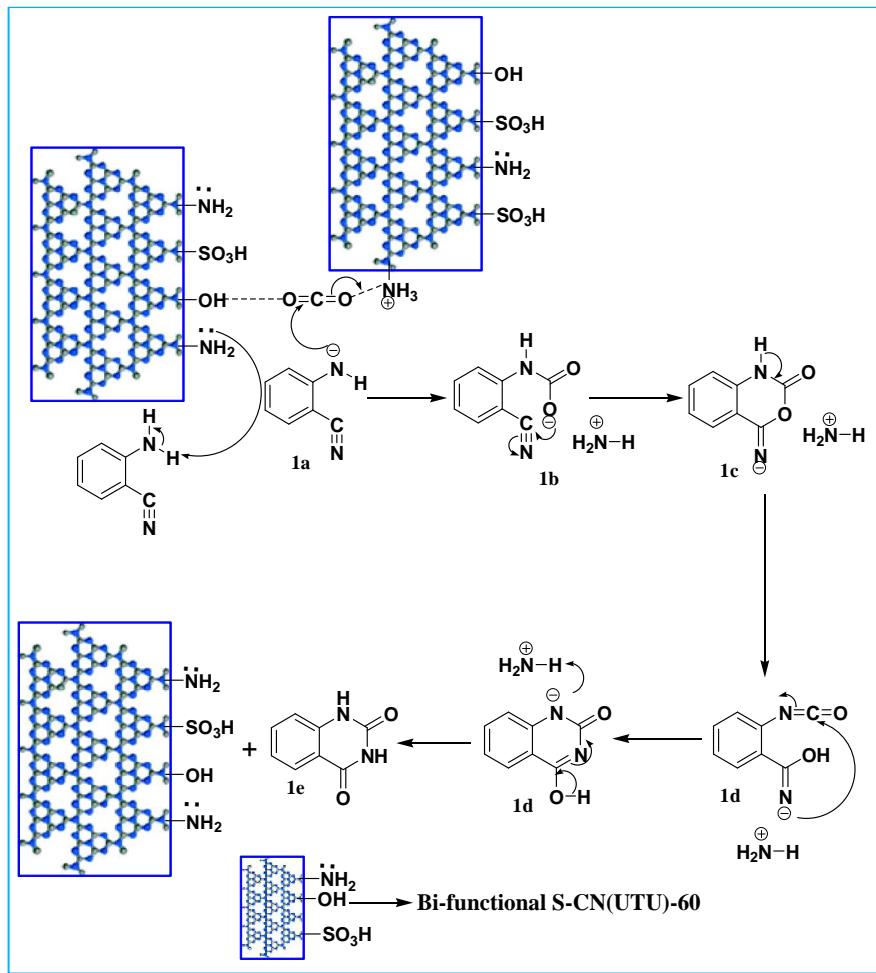
Figure S9. ¹H-NMR spectrum of methyl oleate synthesized from S-CN(UTU)-60.



Scheme S1. Schematic representation for the synthesis methodology and re-evolution of carbon nitride morphology after the H_2SO_4 treatment.



Scheme S2. Proposed mechanism for the synthesis of cyclic carbonate by the cycloaddition reaction of CO₂ and epoxide over bi-functional S-CN(UTU)-60.



Scheme S3. Proposed mechanism for the synthesis of quinazoline-2,4(1H,3H)-dione by the cycloaddition reaction of CO_2 and 2-aminobenzonitrile over bi-functional S-CN(UTU)-60.

References

- [1] R. Srivastava, D. Srinivas and P. Ratnasamy, *Appl. Catal., A*, 2005, **289**, 128-134.
- [2] F. Adam, J. N. Appaturi and E-P. Ng, *J. Mol. Catal. A: Chem.* 2014, **386**, 42-48.
- [3] E. E. Maciasa, P. Ratnasamya and M. A. Carreon, *Catal. Today*, 2012, **198**, 215-218.
- [4] A. Buonerba, A. D. Nisi, A. Grassi, S. Milione, C. Capacchione, S. Vaginc and B. Riegerc, *Catal. Sci. Technol.*, 2015, **5**, 118-123.
- [5] M. Liu, K. Gao, L. Liang, J. Sun, L. Sheng and M. Arai, *Catal. Sci. Technol.*, 2016, **6**, 6406-6416.
- [6] C. M. Miralda, E. E. Macias, M. Zhu, P. Ratnasamy and M. A. Carreon, *ACS Catal.*, 2012, **2**, 180-183.
- [7] R. Srivastava, D. Srinivas and P. Ratnasamy, *J. Catal.*, 2005, **333**, 1-15.