Supporting Information

sp2- and sp3-hybridized Carbon Materials as Catalysts for Aerobic Oxidation of Cyclohexane

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Table S1. Residual metals on carbon materials.

Catalyst	Metal amount (wt%)		
	Mg	Mn	Fe
μ-D	–	–	0.016
nano-D	–	–	0.044
G325	–	–	0.026
G4000	–	–	0.029
r-GO	–	0.225	0.053
meso-G	0.708	–	–

Effect of defects

According to our previous work, annealing the CNTs can efficiently decompose the oxygenous groups and repair the defects, indicated by the decrease of I_D/I_G with annealing temperature. In the free radical reaction, the conversion of C_6H_{12} or ethylbenzene increased with annealing temperature, indicating that CNTs with higher long-range ordering and electron delocalization are preferred.[1-3] We have annealed the meso-G at different temperatures, but no distinct activity was observed (see Table S2), although the ratio of I_D/I_G varied very much. The slight decrease of activity with annealing temperature may be due to the restacking of graphene sheets at high temperatures. Thus, the defects are unlikely to be the major active sites here.

Table S2. CyH oxidation catalyzed by meso-G annealed at 900-1100 °C.[a]

Annealing temperature [d][°C]	I_D/I_G	X[b] [%]	Selectivity[c] [%]			
			KA	CyOOH	AA	GA
900	1.69	21.4	38.6	3.2	50.7	4.2
1100	1.36	20.3	36.9	2.1	46.3	3.7

[a] Conditions: 398 K, 1.5 MPa O_2, 1100 rpm, 14.0 g CyH, 0.39 g Q=O, 9.6 g acetone, 30 mg catalyst. [b] CyH conversion at 8 h. [c] Selectivity of major products at 8 h. KA: cyclohexanol and cyclohexanone, CyOOH: cyclohexyl hydroperoxide, AA: adipic acid, GA: glutaric acid. The by-products included succinic acid, hydroxyl hexylic acid and ε-caprolactone and other undetected acids. [d] The catalyst was annealed for 6h.

Table S3. Effect of solvent on the CyH oxidation catalyzed by meso-G.[a]

Solvent	Oxidant	X[b][%]	Selectivity[c][%]			
			KA	CyOOH	AA	GA
acetone	O_2	22.1	34.4	1.6	53.9	2.3
acetone	—	<1	—	—	—	—
toluene	O_2	15.2	40.2	2.9	43.8	1.8
toluene[d]	O_2	1.5	72.8	8.6	5.8	—

[a] Conditions: 398 K, 1.5 MPa O_2, 1100 rpm, 14.0 g CyH, 0.39 g Q=O, 9.6 g acetone, 30 mg catalyst. [b] CyH conversion at 8 h. [c] Selectivity of major products at 8 h. KA: cyclohexanol and cyclohexanone, CyOOH: cyclohexyl hydroperoxide, AA: adipic acid, GA: glutaric acid. The by-products included succinic acid, hydroxyl hexylic acid and ε-caprolactone and other undetected acids. [d] no catalyst.

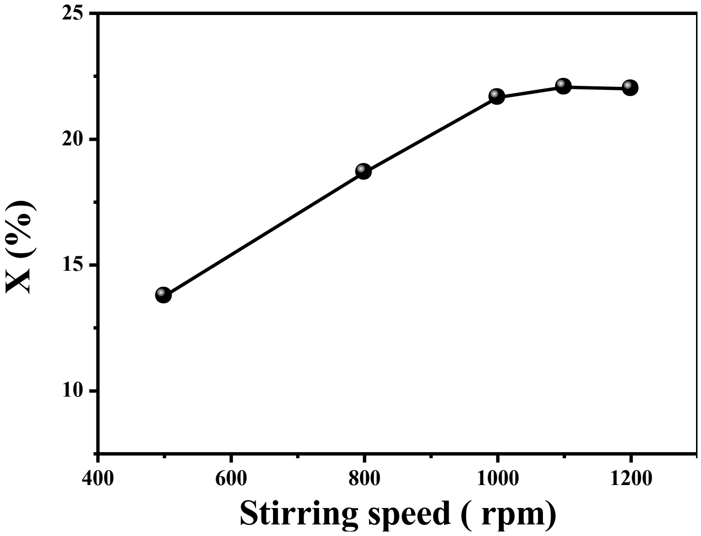

Figure S1.The effect of stirring speed in CyH oxidation catalyze by meso-G.

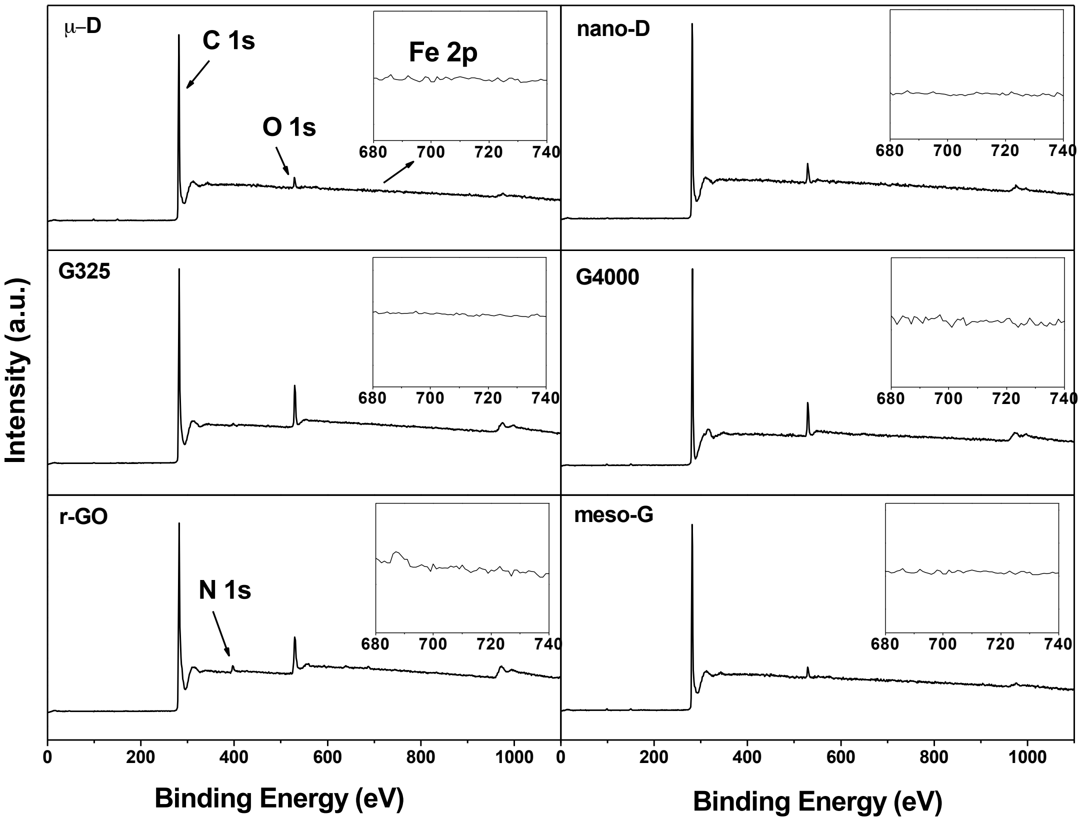

Figure S2. The XPS survey spectrum of carbon materials.

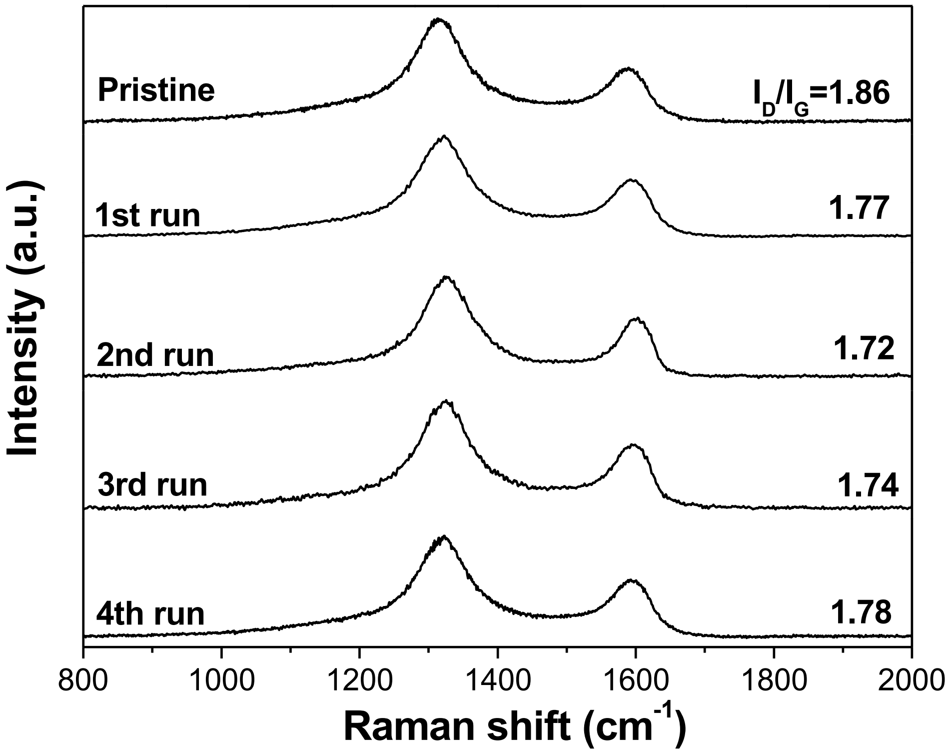

Figure S3. Raman Spectra of fresh and reused meso-G. The similar spectra indicate the structural stability of meso-G in the oxidation of CyH.

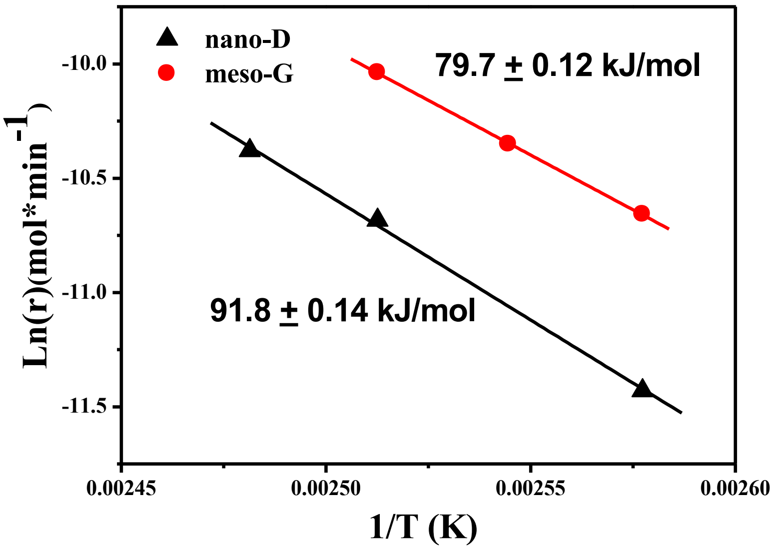

Figure S4. Arrhenius plots of catalytic oxidation of CyH with meso-G and nano-D as catalysts.

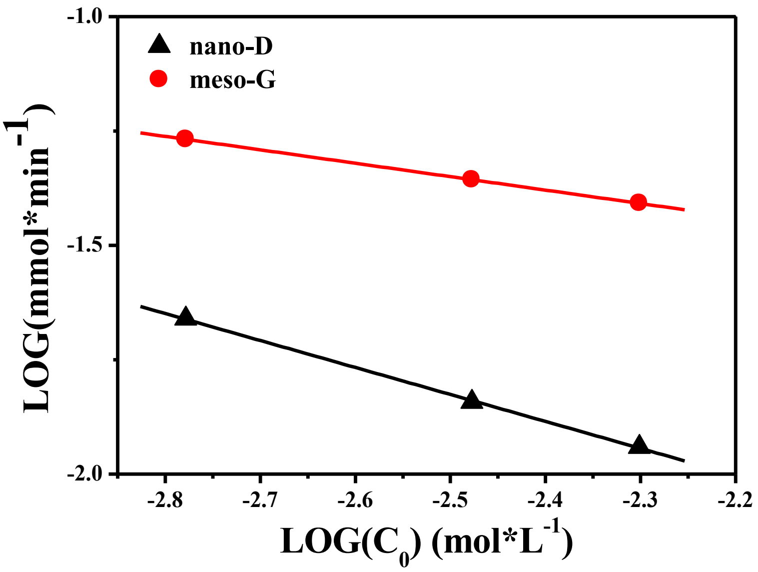

Figure S5. Determination of apparent reaction order of CyH oxidation on substrate.

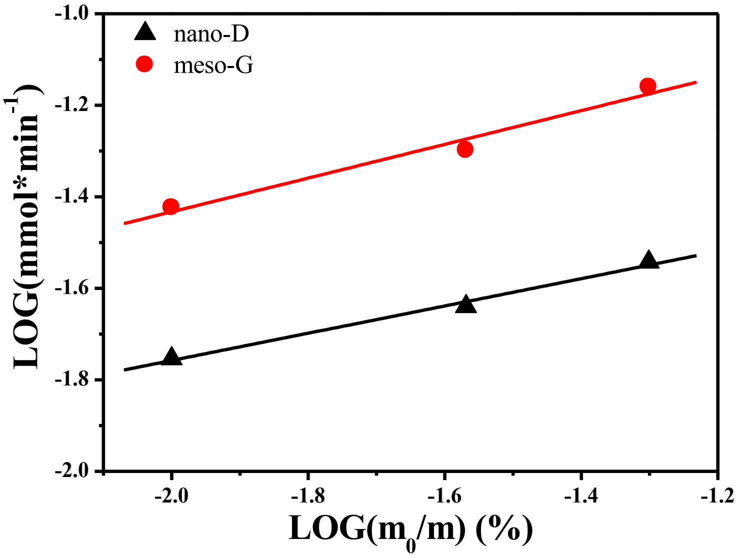

Figure S6. Determination of apparent reaction order of CyH oxidation on concentration of initiator.

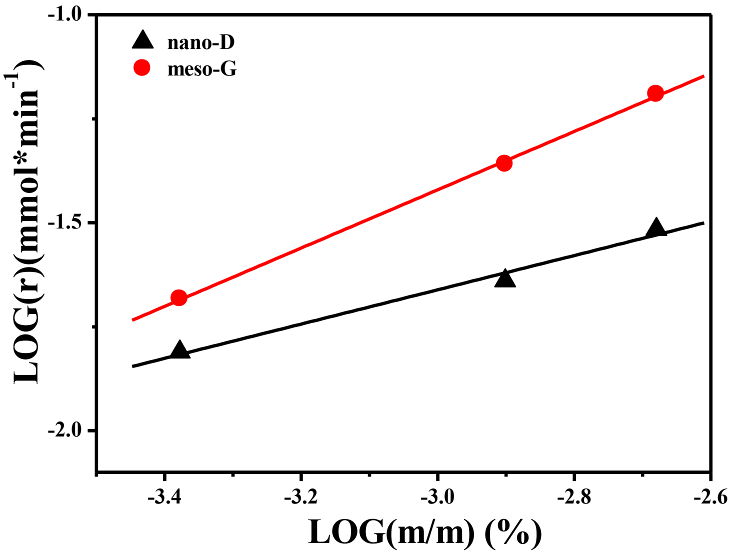

Figure S7. Determination of apparent reaction order of CyH oxidation on concentration of catalyst.

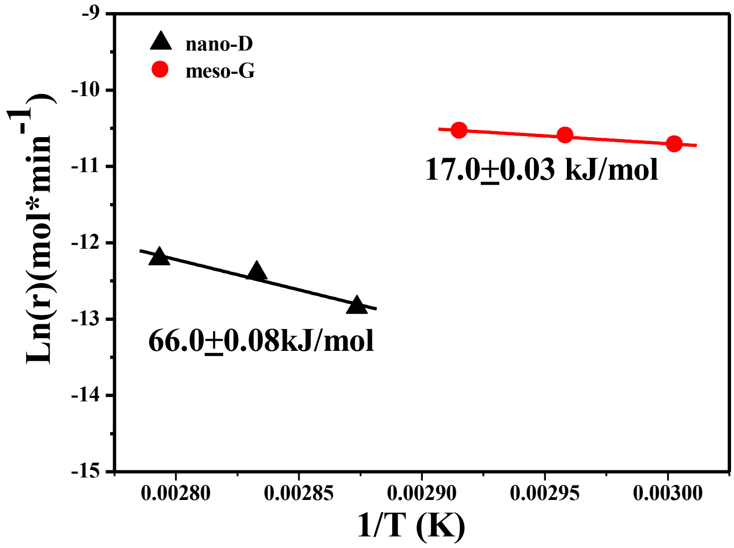

Figure S8. Arrhenius plots of BP decomposition with nano-D and meso-G as catalysts.

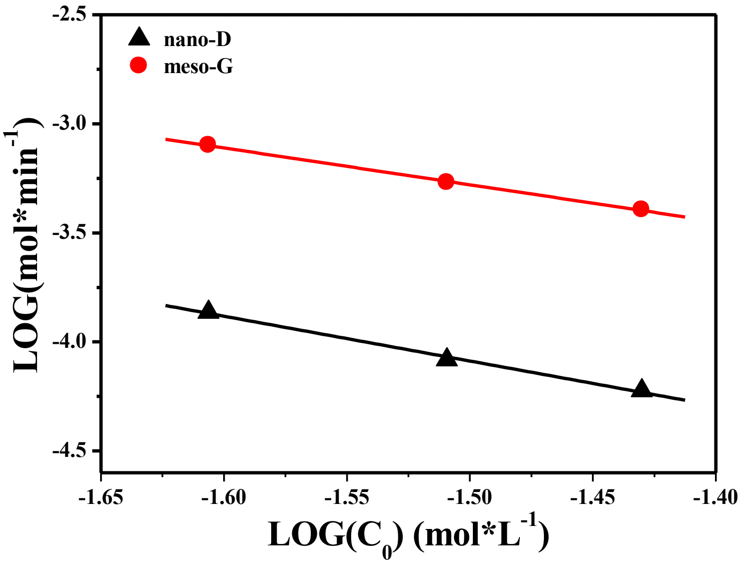

Figure S9. Determination of apparent reaction order of BP decomposition on substrate.

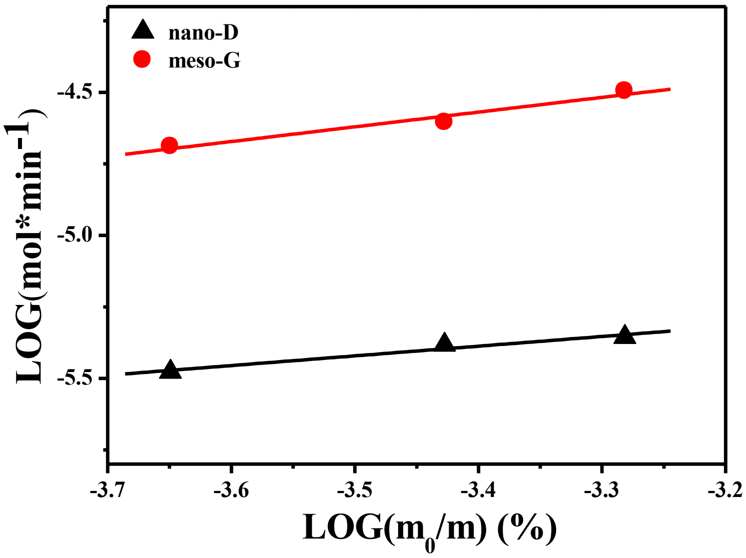

Figure S10. Determination of apparent reaction order of BP decomposition on concentration of catalyst.

References

1 Luo Jin , Peng Feng , Yu Hao , Wang Hongjuan and Z. Wenxu, *ChemCatChem*, 2013, **5**, 1578.

2 Y. Cao, H. Yu, J. Tan, F. Peng, H. Wang, J. Li, W. Zheng and N.-B. Wong, *Carbon*, 2013, **57**, 433.

3 H. Yu, F. Peng, J. Tan, X. W. Hu, H. J. Wang, J. A. Yang and W. X. Zheng, *Angew Chem Int Edit*, 2011, **50**, 3978.