

**Metal-Free Activation of Dioxygen by Graphene/g-C<sub>3</sub>N<sub>4</sub> Nanocomposites:  
Functional Dyades for Selective Oxidation of Saturated Hydrocarbons**

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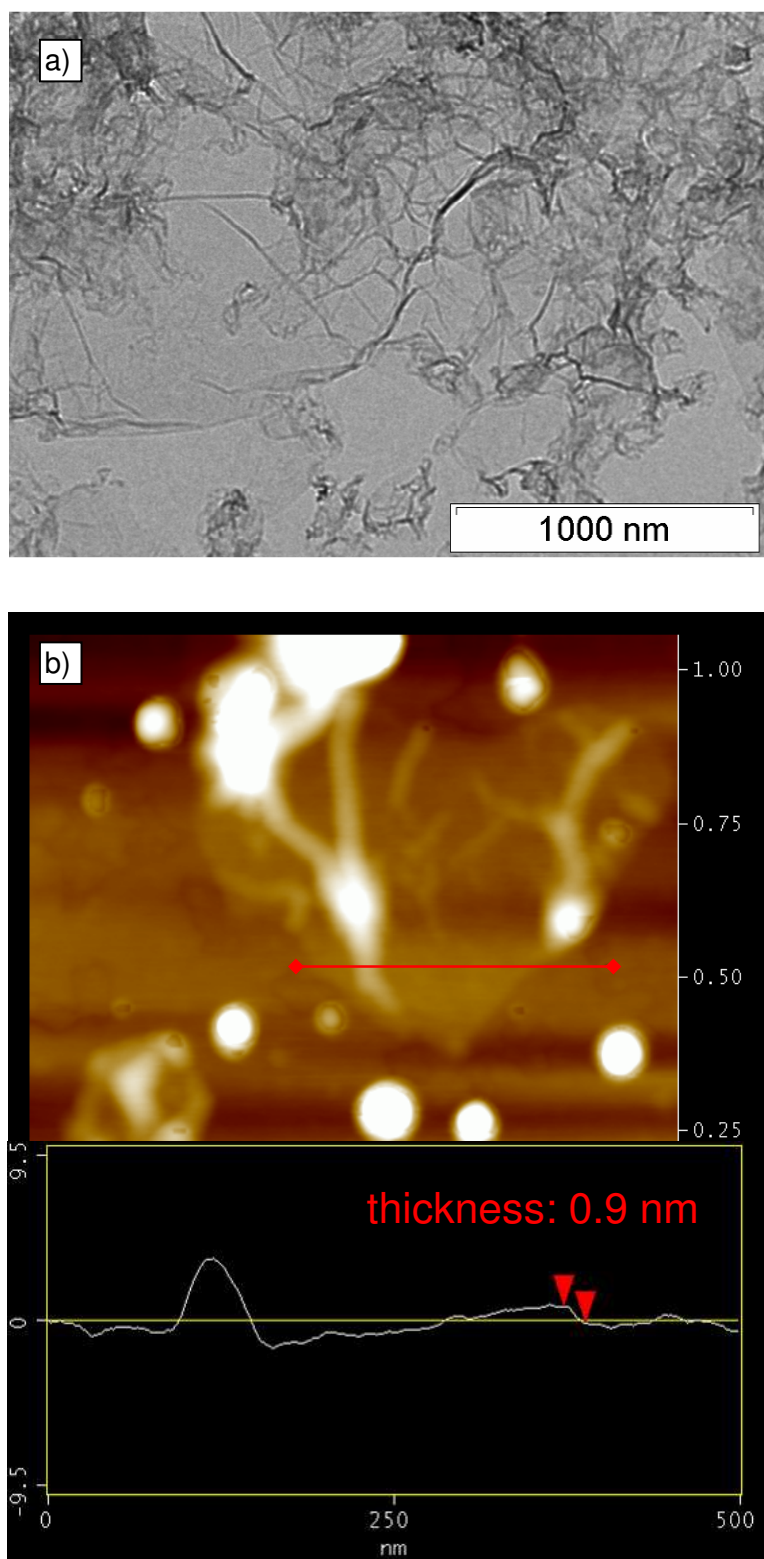
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**Synthesis of GS** Graphene oxide (GO) sheets were synthesized from graphite powder using a modified Hummers method. All chemicals were purchased from Sigma-Aldrich and were used as received. 0.5 g of graphite (1-2 micron), 0.5 g of  $\text{NaNO}_3$ , and 23 mL of concentrated  $\text{H}_2\text{SO}_4$  were stirred together in an ice bath for 1 hour. Next, 3.5 g of  $\text{KMnO}_4$  was slowly added (about 0.1 g/min). Once mixed, the solution was further stirred for another 1 hour in the ice bath and was then heated at  $30 \pm 5$  °C for 30 minutes. After that, 40 ml of water was added into the flask while the temperature was raised to  $90 \pm 5$  °C. After stirring for more 2 hours, 140 mL of water was added, followed by the slow addition of 10 mL of  $\text{H}_2\text{O}_2$  (30%). The warm solution was then filtered and washed with 100 ml of 5% HCl solution and 300 mL of hot water. The remained graphite oxide was redispersed in water by bath-sonication for 30 minutes. Centrifugation was done at 3000 rpm for 30 min to remove all visible particles. The supernatant with a concentration of about 2.8 mg/ml was collected.

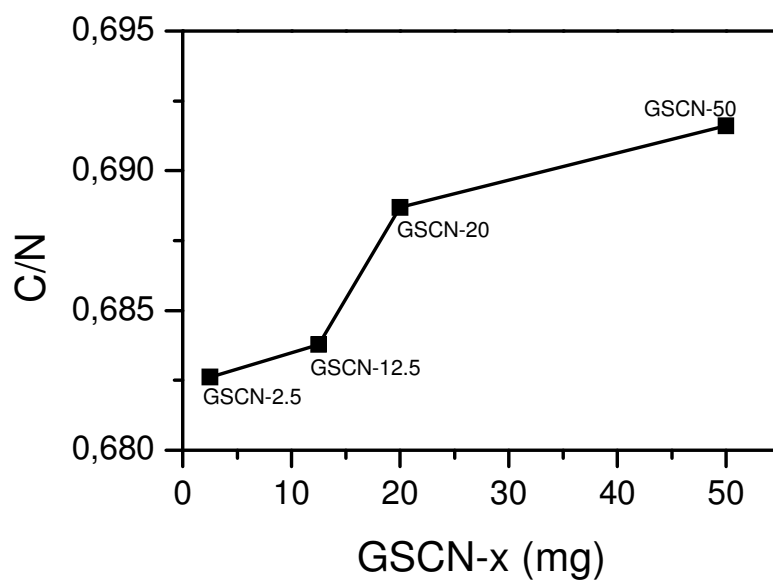
The as-obtained GO solution was diluted with more water to ~0.2 mg/ml. Then, 50 ml of diluted GO solution was sealed in a 100 ml glass bottle and was then irradiated under a 300 W Xenon arc lamp (run time: ~200 hours) for 4 h. Though there is no obvious change in the photo absorption 2 hours later, another 2-hour irradiation is usually applied to ascertain the complete conversion of GO to GS.

**Preparation of GSCN composites** 5 g of cyanamide was dissolved in a certain amount of GO colloidal solution (0.2 mg/ml) and stirred for 10 min. The mixed solution was irradiated with a 300 W Xe lamp for 30 minutes, and then stirred at 80 °C for another 24 h to get grey or black solid. The as-obtained solid was then transferred into a crucible and slowly heated over 4 h to a temperature of 600 °C under the protection of  $\text{N}_2$  flow, and tempered at this temperature for another 4 h. Then, the sample was allowed to cool in the oven to room temperature. Finally, the as obtained green or dark green solid was grinded into fine powder for further use. The yield of GSCN based on cyanamide is around 60 %.

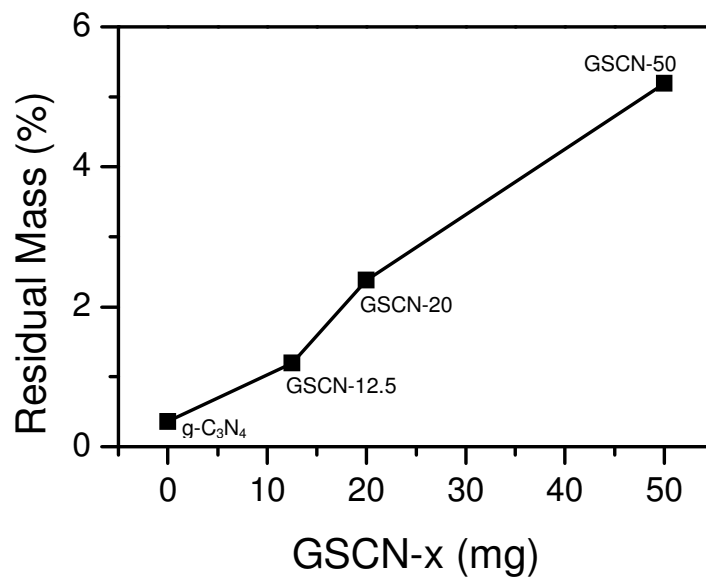
**Preparation of highly reduced r-GO (Gr)** After the centrifugation of as-formed GS solution at a speed of 8000 rpm for 30 min and drying in a vacuum oven at room temperature, the GS powder were obtained. 0.5 g of GS powder was slowly heated over 4 h to a temperature of 600 °C under the protection of  $\text{N}_2$  flow, and tempered at this temperature for another 4 h. Then, the sample was allowed to cool in the oven to room temperature. Finally, the as obtained dark solid was grinded into fine powder for further use.



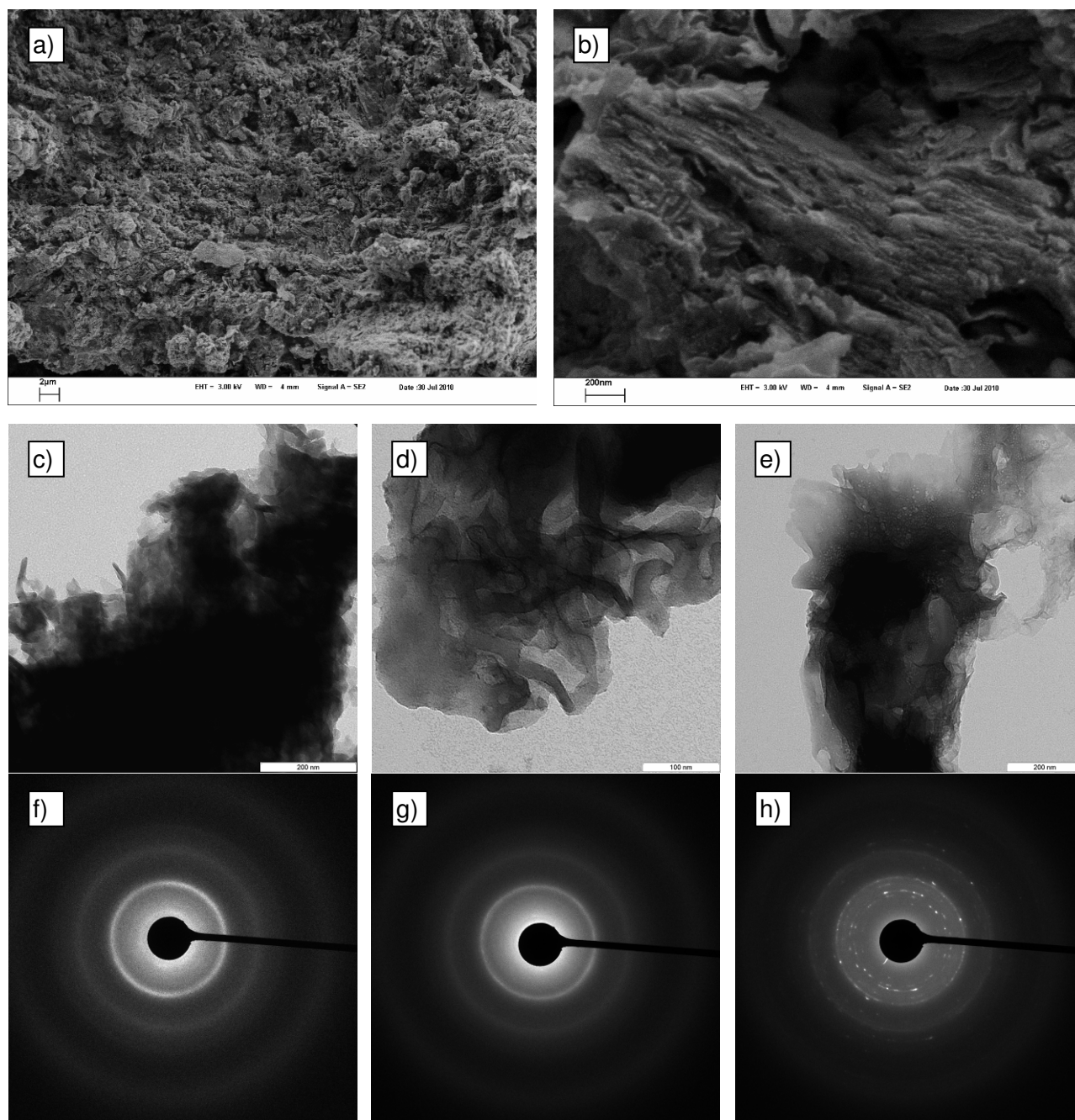
**Figure S1.** TEM (a) and AFM (b) images of GS.



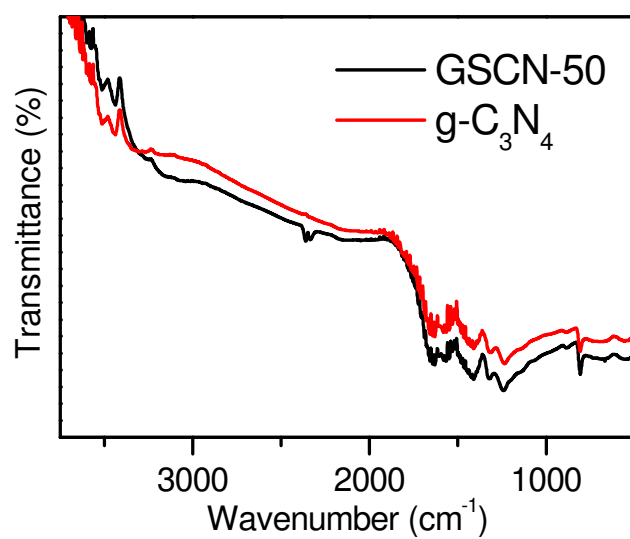
**Figure S2.** The C/N molar ratios of GSCN-x calculated from the elemental analysis results.



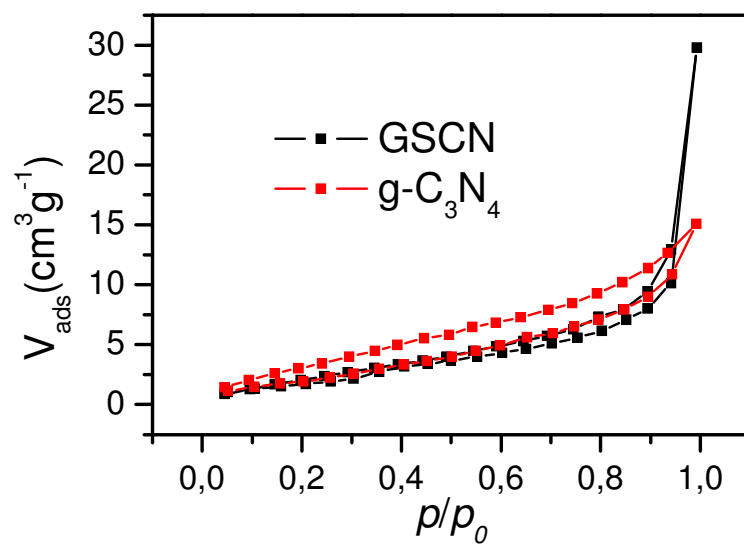
**Figure S3.** The weight percentages of residual mass of g-C<sub>3</sub>N<sub>4</sub> and GSCN-x based on the TG-DTA analysis (20-1000 °C, 10 °C/min, N<sub>2</sub>).



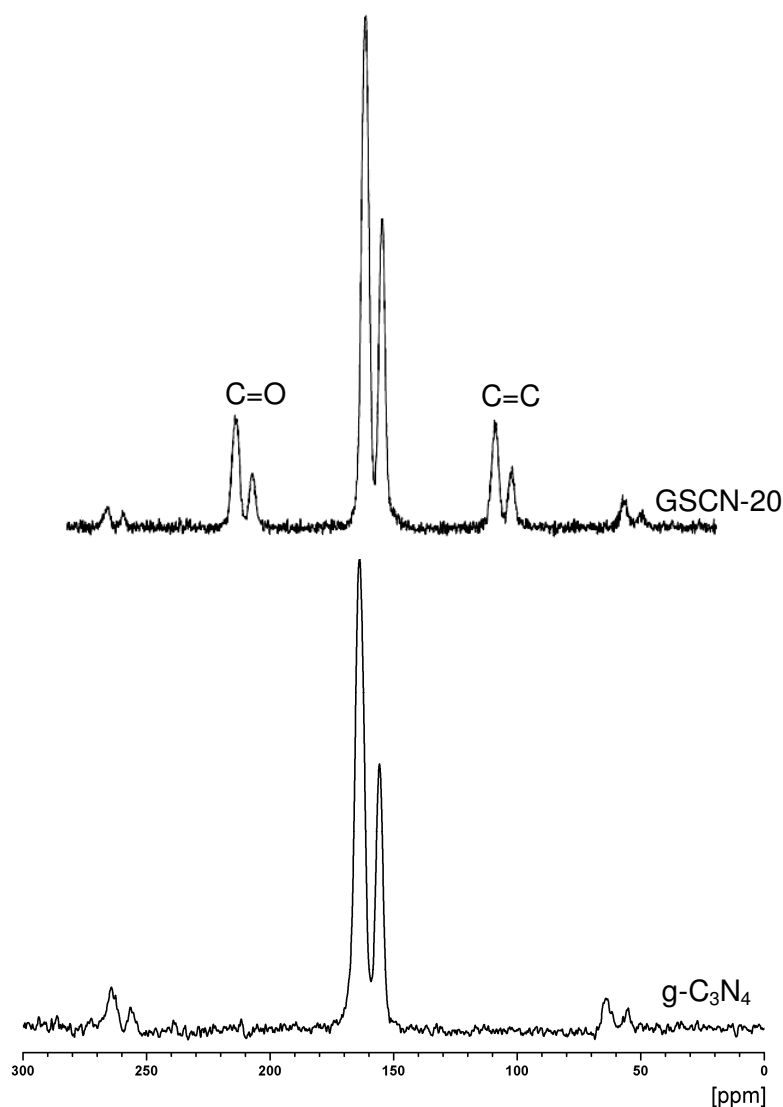
**Figure S4.** SEM (a-b) images of GSCN-20; TEM images and corresponding electron diffraction patterns of g-C<sub>3</sub>N<sub>4</sub> (c, f), GSCN-50 (d, g), and aggregated GS (e, h). The typical electron diffraction pattern of aggregated GS (h) cannot be observed in that of GSCN-50, indicating the homogeneous distribution of monolayer GS in the layered g-C<sub>3</sub>N<sub>4</sub> host.



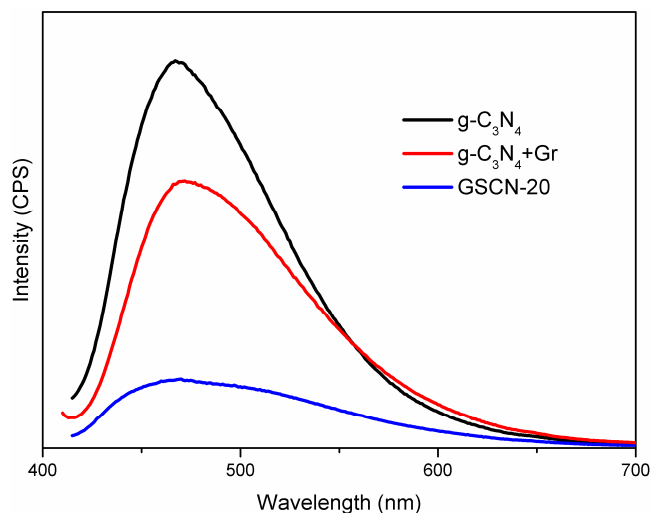
**Figure S5.** FTIR patterns of g-C<sub>3</sub>N<sub>4</sub> and GSCN-50.



**Figure S6.** N<sub>2</sub> adsorption/desorption isotherms of g-C<sub>3</sub>N<sub>4</sub> and GSCN-50.

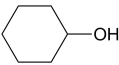
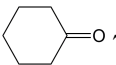
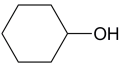
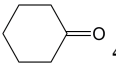
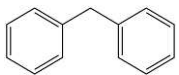
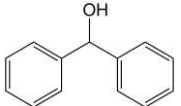
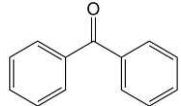
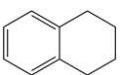
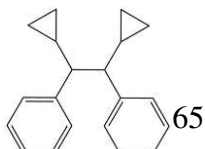
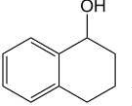
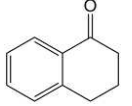


**Figure S7.** Solid-state  $^{13}\text{C}$  magic-angle-spinning (MAS, 10 kHz) NMR spectrum of GSCN-20 and g- $\text{C}_3\text{N}_4$ . Only typical chemical shifts of aromatic carbons (C=C) and carbonyl groups (C=O, aldehydes and ketones) of graphene sheets were observed, excluding the possibility of obvious chemical reaction between GS and other components during annealing. This observation is reasonable as most of surface functional groups of GS have been removed via photochemical reduction before annealing.<sup>ref 9</sup>



**Figure S8.** Photoluminescence spectra of g-C<sub>3</sub>N<sub>4</sub>, GSCN-20, and ground mixture of g-C<sub>3</sub>N<sub>4</sub> (3 g) and highly reduced r-GO (Gr, 50 mg).

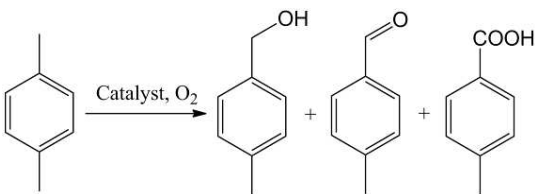
**Table S1.** Reference experiments for selective oxidation of alkanes<sup>[a]</sup>

| Entry            | Substrate                                                                           | Conv. (%) | Main products (Selectivity/%)                                                                                                                                                                                                                                           |
|------------------|-------------------------------------------------------------------------------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 <sup>[b]</sup> |  | 10        |  28  70                                                                                          |
| 2 <sup>[c]</sup> |  | < 1       |  55  45                                                                                          |
| 3 <sup>[d]</sup> |  | 22        |  26  70                                                                                          |
| 4 <sup>[e]</sup> |  | 63        |  65  13  22 |

[a] Conditions: 10 ml CH<sub>3</sub>CN, 10 mmol substrate, 50 mg GSCN-20, O<sub>2</sub> 10 bar, 150 °C, 4h. [b] Solvent-free reaction, 5 ml CHA was added. [c] 10 ml trifluorotoluene was used as the solvent. [d] Reference experiment without catalyst. [e] Reference experiment without catalyst, temperature = 130 °C.

**Catalytic Mechanism** To investigate the underlying activation mechanism of this catalytic system, a series of control experiments were conducted.

**Table S2.** Conversion and selectivity of p-xylene (p-X) oxidation over GSCN catalysts.

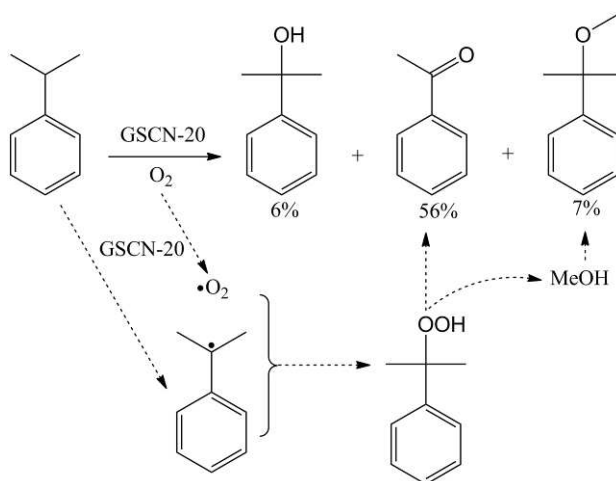


| Catalyst <sup>[a]</sup>         | Conv. (%) | OH(%) | C=O(%) | COOH(%) |
|---------------------------------|-----------|-------|--------|---------|
| g-C <sub>3</sub> N <sub>4</sub> | 17        | 27    | 25     | 48      |
| GS(20 mg)                       | 13        | 31    | 46     | 23      |
| GSCN-2.5                        | 14        | 16    | 48     | 36      |
| GSCN-12.5                       | 15        | 13    | 47     | 40      |
| GSCN-20                         | 33        | 16    | 23     | 61      |
| GSCN-50                         | 22        | 24    | 39     | 37      |
| GSCN-20 <sup>[b]</sup>          | trace     | -     | -      | -       |

[a] Conditions: 10 ml p-xylene, 50 mg catalyst, O<sub>2</sub> 10 bar, 150 °C, 22 h.

[b] The O<sub>2</sub> gas was replaced by N<sub>2</sub> gas.

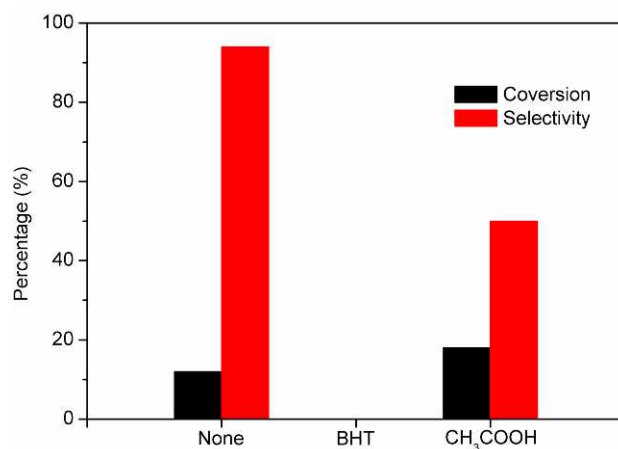
The enhanced oxidation strength of GSCN dyades was also demonstrated in the process of p-X oxidation. GSCN dyades show better catalytic performance in oxidation of p-X to corresponding ketone and acid as compared to that of bare g-C<sub>3</sub>N<sub>4</sub> and GS. Among these catalysts, GSCN-20 gave the highest conversion and also the highest selectivity to corresponding acid, revealing that the introduction of GS into g-C<sub>3</sub>N<sub>4</sub> indeed elevate the oxidation strength of GSCN.



**Scheme S1.** Cumene oxidation over GSCN catalysts.

We also further demonstrated the possibility of the formation of hydroperoxide in O<sub>2</sub>-based catalytic oxidation of cumene. As shown in Scheme S1, catalytic oxidation of cumene in the presence of GSCN-20

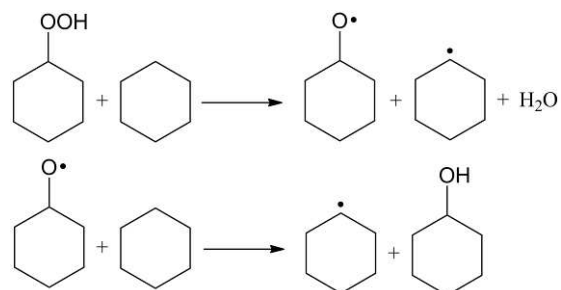
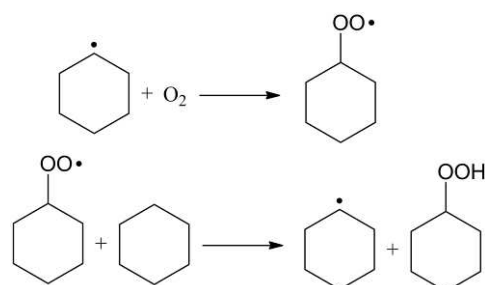
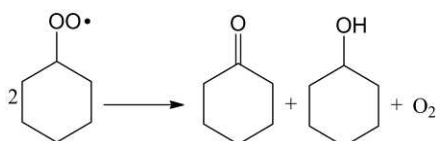
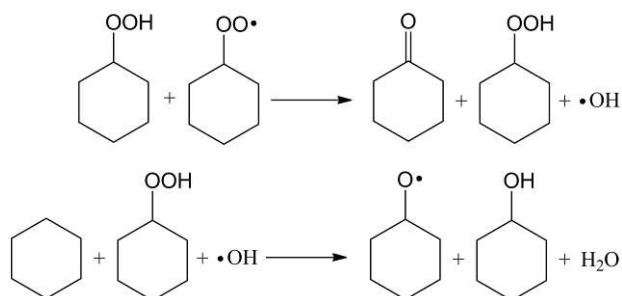
resulted in a conversion of 56% into acetophenone and only a conversion of 13 % to 2-phenylpropan-2-ol and corresponding derivate ((2-methoxypropan-2-yl)benzene). In industry, acetophenone could be obtained via selective decomposition of cumene hydroperoxide with methanol as the byproduct.<sup>S1,2</sup> The formation of both acetophenone and (2-methoxypropan-2-yl)benzene strongly suggests that cumene hydroperoxide formed as the intermediate during the reaction progresses.



**Figure S9.** Effect of additives on the conversion and selectivity of CHA to CHONE catalyzed by GSCN-20. 10 % (molar ratio of substrate) BHT and 200 % CH<sub>3</sub>COOH were applied.

BHT could terminate the oxidation of CHA, further revealing the selective oxidation of CHA processes via  $\bullet\text{O}_2^-$ . However, it is obvious that free  $\bullet\text{O}_2^-$  in solution shows no selectivity in oxidation of various organic substrates. We have previously assumed that  $\bullet\text{O}_2^-$  stays surface-bound to the C<sub>3</sub>N<sub>4</sub> to compensate the positive charge of the hole, resulting in the selectivity of C<sub>3</sub>N<sub>4</sub>-based catalytic system. In the GSCN dyade-based catalytic system, the introduction of CH<sub>3</sub>COOH (2 equals of substrate) could accelerate the conversion rate but lead to the over-oxidation of CHA to corresponding acid products. This observation further reveals the existence of surface-bonded  $\bullet\text{O}_2^-$ , which could be droved by CH<sub>3</sub>COOH into the solution to gain better conversion but as a result worse selectivity to CHO.

After or during the process of the formation hydroperoxides, selective oxidation of CHA was initiated with the help of GSCN dyades via a radical autooxidation mechanism.<sup>S3-5</sup> The proposed autooxidation process as shown in Scheme S2 can be summarized to chain initiation, propagation, and termination steps.<sup>S4-6</sup> CHOL and CHONE were the main products; meanwhile CHOL was further oxidized to CHONE. Under standard conditions (as described in Table 2[a]), the oxidation of CHOL gave a conversion of 95 % with a selectivity of 100 % to CHONE, matching well with the result of the oxidation of CHA (Entry 6 Table 1).

**Initiation step:****Propagation step:****Termination step:****Formation of CHOL and CHONE:****Scheme S2. Proposed autoxidation process of CHA initiated by cyclohexyl hydroperoxide.****Reference:**

- S1 Siegel, H.; Eggersdorfer, M. *Ketones*. Ullmann's Encyclopedia of Industrial Chemistry: 2000.  
 S2 Francisco, M. A. *Chem. Eng. News*, **1993**, 71, 4.  
 S3 Hermans, I.; Nguyen, T. L.; Jacobs, P.; Peeters, J. *ChemPhysChem* **2005**, 6, 637–645.  
 S4 Breynaert, E.; Hermans, I.; Lambie, B.; Maes, G.; Peeters, J.; Maes, A.; Jacobs, P. *Angew. Chem. Int. Ed.* **2006**, 45, 7584–7588.  
 S5 Hermans, I.; Peeters, J.; Jacobs, P. *Top. Catal.* **2008**, 50, 124–132.