Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Title: Room-temperature activation of molecular oxygen over a metal-free triazine-decorated sp2-carbon framework for green synthesis

Authors: Li-Bing Lv, Shi-Ze Yang, Wei-Jie Feng, Wen-Yu Ke, Bing Zhang, Zhi-Dong Jiang, Hong-Hui Wang, Juan Su, Xin-Hao Li, and Jie-Sheng Chen

To be cited as: *ChemCatChem* 10.1002/cctc.201801144

Link to VoR: http://dx.doi.org/10.1002/cctc.201801144

WILEY-VCH
www.chemcatchem.org
A Journal of
ChemPubSoc Europe

10.1002/cctc.201801144

Room-temperature activation of molecular oxygen over a metal-free triazine-decorated sp²-carbon framework for green synthesis

Li-Bing Lv,+ [a] *Shi-Ze Yang,*+ [b] *Wei-Jie Feng,*[a] *Wen-Yu Ke,*[a] *Bing Zhang,*[a] *Hong-Hui Wang,*[a] *Juan Su,*[a] *Xin-Hao Li,**[a] *Zhi-Dong Jiang,* *[a] *and Jie-Sheng Chen*[a]

Dedication ((optional))

Abstract: Additive-free activation of oxygen molecules under ambient conditions has been a great challenge for the green organic synthesis. To make it happen, the design of highly efficient catalyst is the key to make it happen. In this work, we report a simple method to prepare an atomic-scale carbocatalyst via decorating sp^2-carbon framework with triazine (TA-G), which can activate molecular oxygen for highly efficient organic synthesis. Both theoretical and experimental results reveal that TA-G has a Fermi level lied in the middle of the oxygen 2p antibonding orbital of the absorbed O_2 to weaken the O-O bond for room-temperature and additive-free activation of oxygen molecules.

Introduction

The introduction of heteroatoms, e.g. nitrogen, boron or metal elements, is essential to boost the intrinsic activity of sp^2-carbon framework for their potential applications in, not limited to, catalysis and electrocatalysis.[1-4] N-doped nanocarbon as effective electrocatalyst, the "nobility" of N-doped nanocarbons has been well illustrated in pioneering work with improved redox activity by introducing N dopants for oxygen reduction reaction and hydrogen evolution reaction under a suitable work voltage.[5-11] However, N-doped nanocarbon could only provide moderate to good activity for organic synthesis, exemplified with selective oxidation reaction using molecular oxygen, under critical conditions and/or with the presence of scarifying initiators.

The ideal sustainable oxidation process requires a low energy-consuming and zero-emission reaction using green oxidants (e.g. oxygen gas) and reusable catalysts. Theoretical results indicate a large room to modify the electronic structure and thus significantly promote the affinity of adjacent carbon atoms to specific molecules by introducing specific dimers, trimers or even more complex structures of N dopants into the carbon network.[12-16] In combination with the high chemical stability and reusability of nanocarbons, N-decorated nanocarbons complex could principally elevate their affinity and thus depress the activation energy of oxygen molecules even under mild conditions. Developing efficient methods for precise control of specific nitrogen-based chemical structure inside sp^2-carbon lattice is thus the key step to boost the real applications of nanocarbons as effective catalysts for organic synthesis via a green manner.

Herein, we describe the design of triazine decorated graphenes (TA-G) as an atomic-scale carbocatalyst to achieve room-temperature activation of oxygen molecules for organic synthesis (exemplified with oxidative coupling reaction of amine in this work). Both experimental data and theoretical results demonstrated the key role of the triazine rings, rather than separated nitrogen dopants, in significantly enhancing the pre-adsorption of molecular oxygen for desired selective oxidation reaction under ambient conditions.

Results and Discussion

A nano-confinement method[17-20] was modified by carefully optimizing the synthetic temperature to prepare the TA-G samples (Figure 1a and S1). The mixture of glucose and dicyandiamide was thermal-condensed at 600 °C into layered $g\text{-}C_3N_4$ (Figure S1), which can act as a mechanical template to confine carbonaceous intermediates in their interlayer space for further carbonization into patched graphenes at elevated temperatures. The $g\text{-}C_3N_4$ also acted as a chemical template to release melem, triazine and other gaseous species at a temperature higher than 750 °C (Figure S1) for further hybridization with graphenes. The two dimensional structure of the TA-G sample was directly observed by the scanning electron microscopy (SEM) (Figure S1) and transmission electron microscopy (TEM) (Figure S2) images. The mean thickness of primary sheets in TA-G sample was estimated by the height analysis of atomic force microscope (AFM) measurement (Figure 1b and S3) to be between 0.83 and 1.12 nm, from which infer the presence of a hydrated graphene-like monolayer.[21] Indeed, the single step (red lines in Figure 1b) of multisheet structures exhibits a measured thickness of 0.42 nm, comparable to that of ideal graphene (0.34 nm). As expected, the TA-G aerogel has a high specific surface area (777.7 $m^2\,g^{-1}$) according to the N_2 adsorption analysis results (Figure S4). The metal-free feature of TA-G sample was confirmed by X-ray photoelectron spectroscopy (XPS) results (Figure S5-8) with only C, N and O signals detected. Corresponding powder X-ray diffraction (XRD) pattern (Figure S9) exhibited rather broad diffraction peaks of graphite. The possibility of a significant amount of $g\text{-}C_3N_4$ residual in the TA-G sample was

---

[a] L.-B. Lv, W.-J. Feng, W.-Y. Ke, B. Zhang, H.-H. Wang, Dr. J. Su, Prof. X.-H. Li, A.P. Zhi-Dong Jiang, Prof. J.-S. Chen
School of Chemistry and Chemical Engineering
Shanghai Jiao Tong University
Shanghai 200240 (P. R. China)
Fax: +86-21-54741297
E-mail: xinhaoli@sjtu.edu.cn; zdjiang@sjtu.edu.cn

[b] Dr. S.-Z. Yang +
Materials Science and Technology Division,
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6201, United States

\+ These author contributed equally to this work.
Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

10.1002/cctc.201801144

excluded by the Raman observation (Figure S10) without obvious photoluminescence signal in the background. The triazine rings could be observed in the high resolution scanning transmission electron microscopy (HR-STEM) annular dark field (ADF) images (Figure 1c, d and S13) with the schematic structure depicted in Figure 1e. The element mapping high-angel annular dark field (HAADF) image (FigureS12) revealed the homogeneous distribution of nitrogen dopants in the carbon layers mainly in the form of sp^2-bonded N, as demonstrated by the electron energy loss spectra (EELS) (Figure 1f).

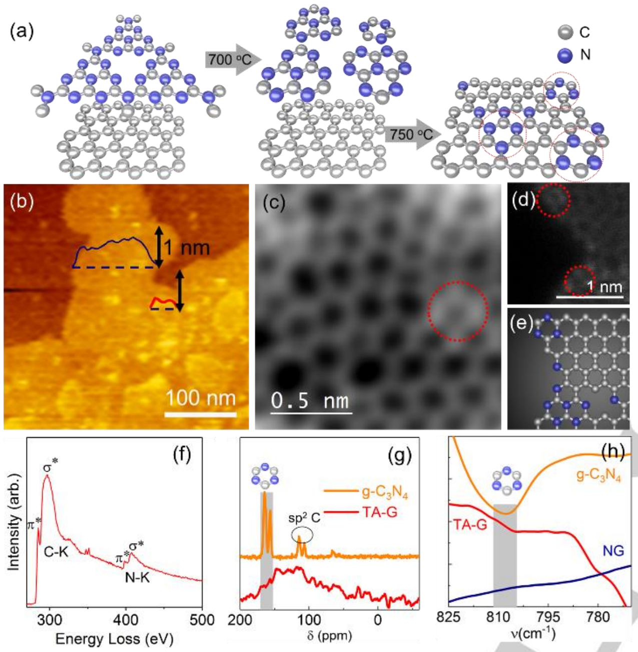


Figure 1. (a) The synthetic process of TA-G from thermal condensation of glucose and dicyandiamide with g-C_3N_4 (upper left) formed at 600°C as chemical and mechanical templates. (b) AFM image of TA-G deposited on freshly cleaved mica and corresponding height analysis results. STEM-ADF (c-d) images and corresponding schematic structure (e) of TA-G sample. EELS (f), ^{13}C solid state NMR (g) and FTIR (h) spectra of TA-G and control samples.

The presence of trianzine rings in TA-G sample was further confirmed by the solid nuclear magnetic resonance (NMR) of ^{13}C, directly convincing the existence of triazine rings in TA-G with typical signals the same with those of triazine subunits in g-C_3N_4 sample (Figure 1g).[22,23] The breathing mode of the triazine rings with a typical fourier transform infrared spectroscopy (FTIR) peak around 800 cm^{-1} (Figure 1h and S14) further demonstrated the integration of triazine rings in the TA-G sample. Such a breathing mode peak disappeared in the FTIR spectra of nitrogen doped graphene (NG, sample obtained at 900 °C) and graphene (Gr, sample obtained at 900 °C) samples obtained at high temperatures (>900 °C), suggesting the heat-induced deconstruction of the triazine rings (Figure S14).

The introduction of trianzine subunits also lead to appropriate band gap. The ultraviolet photoelectron spectroscopy (UPS) (Figure 2a, b and S11) suggests a much lower valence band position. The band gap of TA-G (Figure 2d) is estimated to be 0.91 eV based on the UPS results and Mott-Schottky plots (Figure 2c), revealing an enhanced redox power by introducing triazine subunits. The variation in the band gap of TA-G is a typical indicator of the effect of nitrogen dopants and the triazine rings on the modified electronic structure of the carbon framework. Moreover, the lowered the VB (or HOMO) or elevated the CB (or LUMO) could induce electron relocalization at the interface of the substrate/oxygen molecules and TA-G and thus activate these reactants for further oxidation reactions.

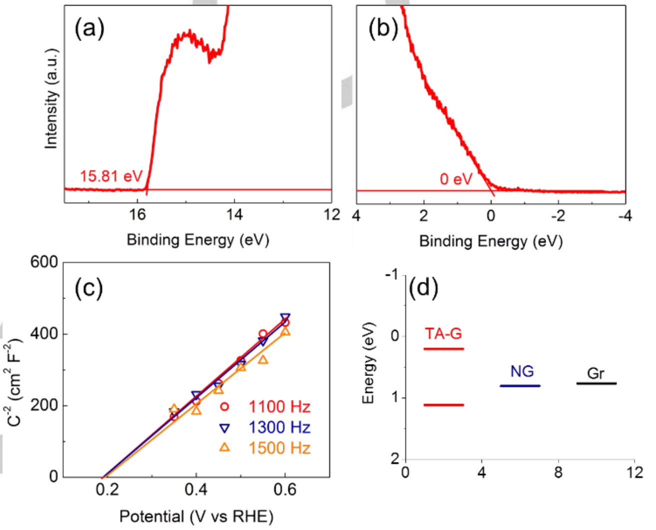


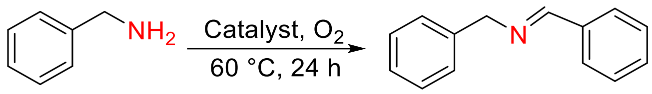
Figure 2. UPS spectra in the cutoff (E_{cutoff}) (a) and the onset (E_i) (b) energy regions of TA-G. (c) Mott-Schottky plots for TA-G at different frequency. (d) The conduction band (CB) and valence band (VB) position of TA-G, NG and Gr are calculated based on the UPS and Mott-Schottky plots.

Enlightened by the unique chemical and band structure of TA-G, we initially examined its catalytic performance of activating oxygen gas for organic synthesis under mild conditions. The oxidative coupling reaction of amines is a typical model reaction for evaluating the catalytic performance of various carbonaceous catalysts.[24-26] We thus selected the oxidation of benzylamine as a model reaction by using N'N-dimethylacetamide as the optimal solvent (Table S1) and oxygen gas as the oxidant to test the possibility of TA-G as carbocatalysts without the assistance of any other additives. As shown in Table 1, oxygen gas could not be activated to oxidize the benzyl amine without the involvement of a catalyst at 60 °C. As the state-of-the-art metal-free catalyst, the boron and nitrogen co-doped graphenes (BNHG) could give a moderate conversion (40 %) and a good selectivity of 94% to n-benzylidenebenzylamine. Moderate conversions were also archieved by the control samples NG and Gr with more or less nitrogen dopants. The TA-G catalyst offered the highest conversion of benzylamine (93%) and excellent selectivity to imine (>99%) among the used control sample (Table 1 and S3), rather suggesting the important effect of the triazine units on accelerating the activation of oxygen gas.

10.1002/cctc.201801144

In a further set of experiments, we examined the general efficacy and functional-group tolerance of TA-G under the typical reaction condition for selective oxidation of substituted benzylamines (Figure S16) with both electron-withdrawing (-Cl, -CF_3) and electron-donating (-CH_3, -OCH_3) functional groups. TA-G could smoothly trigger the oxidative coupling of most substituted benzylamines with excellent conversion and selectivity. The steric effect decreased the conversion of 2, 5-dimethoxybenzylamine towards corresponding imines. All these results suggested the importance of the pre-adsorption of the substrate molecules on the surface of TA-G for the mild and efficient oxidation reactions. A conversion of 64% for heterocyclic amines 2-thiophenemethylamine over the TA-G catalyst with a high selectivity (99%) further suggests the good compatibility of the TA-G catalyst to sulphur heteroatoms, which are usually toxic species to the metal-based catalysts.

Table 1. Study of reaction conditions.



Entry	Catalyst	T (°C)	Conv.(%)	Sel. (%)
1	--	60	--	-
2	BNHG	60	40	94
3	TA-G	60	93	99
4	NG	60	47	99
5	Gr	60	36	99
6	mpg-C_3N_4	60	33	99
7	g-C_3N_4	60	6	99
8	TA-G	27	42	98
9[a]	TA-G	60	75	59

Typical reaction conditions: 40 mg of catalyst, 5 mL of N'N-dimethylacetamide, 0.5 mmol benzylamine, 1 bar O_2, 24 h. [a] 100 mol% acetic acid was added, the only byproduct was N-acetylbenzylamine (selectivity 41%).

As the only sample containing an obvious amount of triazine rings, the TA-G exhibited unexpected room-temperature activity to trigger the selective oxidation of benzylamine using oxygen gas without the assistance of additives or light irradiation. At a temperature of 27 °C, In order to demonstrate remarkable activity of TA-G catalyst to activate molecular oxygen for organic synthesis, we investigated the electronic partial density of states (PDOS) and adsorption energies of different calculation models (Figure S15) on the basis of possible structures of nitrogen heteroatoms in the TA-G sample. As expected, the TA-G sample has the strongest interaction with O_2 molecule and thus the highest adsorption energy of oxygen (Figure 3f) to further stimulate their chemical reactivity for various reactions. TA-G could activate oxygen (1 bar) for the transformation of benzylamine (Figure 3a), offering a conversion of 42% and a good selectivity to imines (98%) in 24 h and nearly a complete conversion with constant selectivity (97%) within 9 days. The turn over frequency (TOF) value of TA-G (Figure 3b) was calculated to be 0.202 h^{-1}, whilst the TOF values of NG and Gr are negligible under fixed conditions.

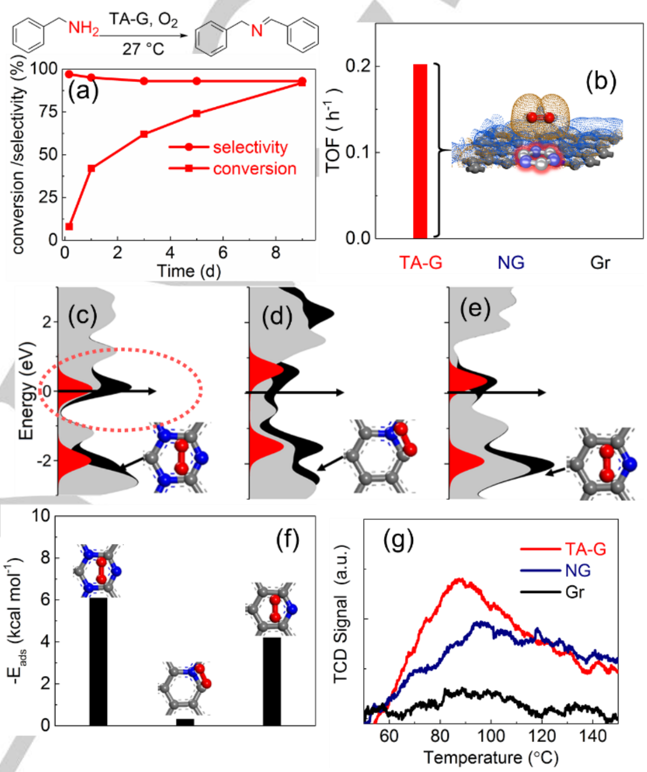


Figure 3. Room-temperature oxidation (a) of benzylamine over TA-G and corresponding TOF values (b) as compared with NG and Gr catalysts. TOF was calculated on the basis of the conversions (8%) at 4 h. Reaction conditions: 40 mg of TA-G, 5 mL of N'N-dimethylacetamide, 0.5 mmol benzylamine, 1 bar O_2, 27 °C. The electronic partial density of states (PDOS) for theoretical models of triazine- (c), graphitic nitrogen- (d) and pyridinic nitrogen- (e) decorated graphenes and calculated adsorption energy (f) for oxygen molecule; black area: the interaction between oxygen and catalyst; gray: the catalyst model; red: the adsorbed oxygen molecule. For detailed calculation models please see Figure S15. (g) O_2-TPD results of TA-G, NG and Gr.

Indeed, there is a big difference in the band structures of different C-N complex-based samples (TA-G, NG and Gr) according to the UPS and Mott-Schottky plots (Figure 2 and S11), matching well with the simulation results (Figure 3c-e and S15). Most importantly, careful investigation on the PDOS plots of TA-G (Figure 3c) showed a significant change in the position (black arrows in Figure 3c-e) of fermi level of the absorbed O_2 orbitals (Figure 3c red) over different C-N complexes. The fermi level lies in the middle of the oxygen 2p antibonding orbital of the triazine-absorbed O_2 (Figure 3c red), indicating an obvious weakening of the O-O bond due to its strong interaction with the triazine-based catalyst.[15]

However, only integrated triazine units in the graphene layers could ensure the high catalytic activity via forming unique CN complexs, as already demonstrated by the theoretical results (Figure 3). Indeed, g-C_3N_4 and mpg-C_3N_4 (entries 3-4, Table 1), composed of triazine rings as the main subunits with varied surface areas, could trigger this reaction and only gave moderate conversions of 6% and 33%, respectively, under fixed conditions. The fact that the mpg-C_3N_4 sample with a much higher content of triazine subunits (> 30 times of the TA-G sample) could only give one third of the activity of TA-G sample, rather suggests the key importance of the integrated structure of the triazine rings inside the carbon framework for facilitating the activation of the reactants in this work.

In order to further glean the real role of the TA-G catalyst in activating the molecular oxygen, we carried out a series of quenching experiments (Table S2) with the involvement of a certain amount of butylated hydroxytoluene (BHT), carotene and catalase as specific scavengers for possible active oxygen species, including superoxide radical, $^1O_2$ and H_2O_2, respectively.[27-31] The failure of all these scavengers to quench the oxidation of benzylamine over TA-G excluded the possibility of the formation of free superoxide radical, $^1O_2$ and H_2O_2 in the reaction process. Further addition of 1 equal of acetic acid to the catalytic system could, however, obviously depress the conversion from 93% to 75% (Entry 9, Table 1) and disturb the selective oxidative coupling reaction with a selectivity of 41% to acetylbenzylamine. Acetic acid could remove possible surface-absorbed oxygen-species, resulting in an obviously decreased conversion. Obviously, the strong base-acid interaction of acetic acid and the triazine ring could protonate the triazine-based complexes in the TA-G catalyst, the proposed active sites for the activation of molecular oxygen according to the theoretical results (Figure 3 and S15), and thus depress the pre-adsorption of oxygen molecules for further oxidations process, resulting in a much lower selectivity to the oxidation product (59%). The direct contribution of the triazine-based complexes in the TA-G catalyst to the promoted catalytic activity has been well reflected by a strong and novel peak in the CO_2 temperature-programmed desorption (CO_2-TPD) profile of TA-G (Figure S17) at low-temperature range as compared with those of NG and Gr samples, even though the nitrogen contents of TA-G is comparable to that of NG (Figure S18). Such a new type of active Lewis base cites in the TA-G catalyst significantly enhance the adsorption capacity of oxygen with a strong peak of O_2-TPD profile at 90 ° C (Figure 3g), matching well with the trend of the calculated absorption energy of O_2 (Figure 3f) over different C-N complexes.

Finally, the good reusability of the TA-G catalyst was also carefully analysed by recycling the used catalyst for further reactions. Slight decrease in the activity of the used TA-G catalyst was mainly caused by the gradual loss of the TA-G sample during the centrifugation and washing process after the reaction. Nevertheless, the TA-G kept a constant conversion through overtime (Figure S19) suggesting the stability of the triazing-based active centers for multiple cycles of reuses.

Conclusions

In conclusion, we described the synthesis of triazine-decorated graphenes (TA-G) as an atomic-scale carbocatalyst for room-temperature activation of oxygen molecules for selective oxidation. The unique C-N complexes forming by the combination of triazine and atom-thick structure significantly endowed TA-G the capability to activate oxygen at room temperature by enhancing the pre-adsorption of oxygen molecules over the triazine-carbon complexes as demonstrated with both the theoretical and experiments results. We proposed a novel strategy to modify the graphene for the design of novel and functional carbocatalysts with great application potentials in various realms of green chemistry and synthesis.

Experimental Section

Synthesis of TA-G: A mixture of dicyandiamide, glucose (mass ratio of dicyandiamide and glucose was 40:1) were dissolved in deionized water and stirred in an opened beaker at 80 °C for 24 h to remove water. The resulting white powder was heated to 750 °C at a rate of 2.4 °C min^{-1}, held at that temperature for 2 h under the protection of N_2 flow (20 mL min^{-1}), and cooled down to room temperature. The as-obtained material was directly used for characterization and further experiments.

Synthesis of NG or Gr: A mixture of dicyandiamide, glucose (mass ratio of dicyandiamide and glucose was 40:1) were dissolved in deionized water and stirred in an opened beaker at 80 °C for 24 h to remove water. The resulting white powder was heated to 900 °C (for NG) or 1000 °C (for Gr) at a rate of 2.4 °C min^{-1}, held at that temperature for 1 h under the protection of N_2 flow (20 mL min^{-1}), and cooled down to room temperature. The as-obtained materials were directly used to characterization and further experiments.

Synthesis of BNHG: A mixture of dicyandiamide, glucose and boric acid (mass ratio of them was 40:1:0.4) were dissolved in deionized water and stirred in an opened beaker at 80 °C for 24 h to remove water. The resulting white powder was heated to 600 °C at a rate of 2.4 °C min^{-1} and at this temperature for another 2 h under a flow of nitrogen. The material was then heated further at a rate of 3.3 °C min^{-1} to 1000 °C and maintained at that temperature for 1 h. The sample was cooled down to room temperature. The as-obtained material was directly used to characterization and further experiments.[17]

Synthesis of g-C_3N_4: Dicyandiamide was heated to 600 °C at a rate of 2.4 °C min^{-1}, held at that temperature for 2 h under the protection of N_2 flow (20 mL min^{-1}), and cooled down to room temperature. The as-obtained material was directly used to characterization and further experiments.

Synthesis of mpg-C_3N_4: A mixture of cyanaminde, Ludox HS40 solution (dispersion of 12 nm SiO_2 particles with 40 wt% in water) (mass ratio was 5:7.5) was heated at 65 °C in an opened beaker for 24 h to remove water. The as-formed white powder was heated to 600 °C at a rate of 2.3 °C min^{-1} under the protection of N_2, and held at that temperature for 4 h. The resulting brown-yellow powder was treated with a 4 M HF acid for 24 h to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol. After that, the powders were dried at 60 °C in vacuum overnight. The as-obtained material was directly used to characterization and further experiments.

Typical reaction conditions: 0.5 mmol of benzylamine, 40 mg of catalyst, 5 mL of solvent, 60 °C for 24 h, 1500 rpm, 1 bar O_2. The products were qualified with n-hexadecane as an internal standard under typical reaction conditions and were detected by GC-MS. The carbon balance was estimated to be 94 % ~ 96 %.

Room temperature Reaction conditions: 40 mg of TA-G, 5 mL of N'N-dimethylacetamide, 0.5 mmol benzylamine, 1 bar O_2, 1500 rpm, 27 °C.

Turn over frequency (TOF):

$$\mathrm{TOF} = n_s * \frac{Conversion}{n_{act} * Time}$$

n_s represents the mole of substrate, n_{act} represents the mole of active cites. The amount of active cites (triazine rings) was calculated from the changed nitrogen contents from TA-G to Gr based on the XPS analysis results.

The quenching reaction: Butylated hydroxytoluene (10 times of substrate in mol%) was added to the reaction system with solvent and catalyst. The mixture was stirred for 2 h to get a homogeneous dispersion before substrate was added. Then the reaction was carried out for 24 h at 60 °C under 1 bar oxygen.

The effect of carotene or catalase: 2 mg of carotene or equal mol of catalase was added to the reaction system with solvent and catalyst before the substrate was added. Then the reaction was carried out for 24 h at 60 °C under 1 bar oxygen..

Acknowledgements ((optional))

This work was supported by National Natural Science Foundation of China (21720102002, 21722103 and 21673140), Shanghai Basic Research Program (16JC1401600), Shanghai Eastern Scholar Program and Shanghai Rising-Star Program (16QA1402100) and SJTU-MPI partner group.

.

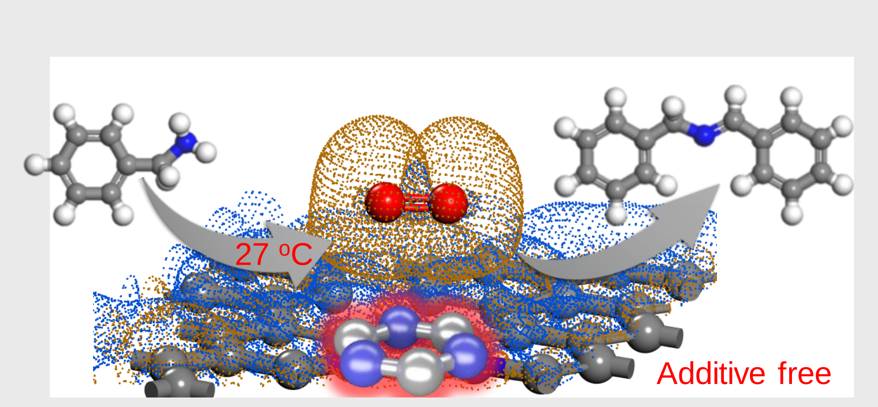
Keywords: triazine • grafting • sp^2-carbon framework • selective oxidation

[1]. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
[2]. G. Liu, A. W. Robertson, M. M.-J. Li, W. C. H. Kuo, M. T. Darby, M. H. Muhieddine, Y.-C. Lin, K. Suenaga, M. Stamatakis, J. H. Warner, S. C. E. Tsang, *Nat. Chem.* **2017**, doi:10.1038/nchem.2740.
[3]. C. Hu, L. Dai, *Adv. Mater.* **2016**, *29*, 1604942.
[4]. H. Liu, Y. Liu, D. Zhu, *J. Mater. Chem.* **2011**, *21*, 3335.
[5]. H. Wang, T. Maiyalagan, X. Wang, *Acs Catal.* **2012,** *2,* 781.
[6]. Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D. S. Su, J. Wang, X. Bao, D. Ma, *Angew. Chem. Int. Ed.* **2013**, *52,* 2109; *Angew. Chem.* **2013,** *125,* 2163.
[7]. T. P. Kaloni, R. P. Joshi, N. P. Adhikari, U. Schwingenschlögl, *Appl. Phys. Lett.* **2014,** *104*, 073116.
[8]. R. Nascimento, J. d. R. Martins, R. J. C. Batista, H. Chacham, *The J Phys. Chem. C* **2015,** *119,* 5055.
[9]. Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, *J. Am. Chem. Soc.* **2014,** *136*, 4394.
[10]. Y. Jiao, Y. Zheng, K. Davey, S.-Z. Qiao, *Nat. Energy* **2016,** 1, 16130.
[11]. D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science* **2016,** *351,* 361.
[12]. Z. Hou, X. Wang, T. Ikeda, K. Terakura, M. Oshima, M.-a. Kakimoto, S. Miyata, *Phys Rev B* **2012,** *85,* 165439.
[13]. C. Pu, D. Zhou, Y. Li, H. Liu, Z. Chen, Y. Wang, Y. Ma, *The J. of Phys. Chem. C* **2017,** *121*, 2669.
[14]. G.-L. Chai, Z. Hou, D.-J. Shu, T. Ikeda, K. Terakura, *J. Am. Chem. Soc.* **2014,** *136,* 13629.
[15]. P. J. Van den Hoek, E. J. Baerends, R. A. Van Santen, *J. Phys. Chem.* ***1989,*** *93,* 6469.
[16]. M. Antonietti, M. Oschatz, *Adv Mater*, **2018,** DOI: 10.1002/adma.201706836.
[17]. X. H. Li, M. Antonietti, *Angew. Chem. Int. Ed.* **2013**, *52,* 4572; *Angew. Chem.* **2013,** *125,* 4670.
[18]. X. H. Li, S. Kurasch, U. Kaiser, M. Antonietti, *Angew. Chem. Int. Ed.* **2012**, *51*, 9689; *Angew. Chem.* **2012,** *124,* 9827.
[19]. L.-B. Lv, T.-L. Cui, B. Zhang, H.-H. Wang, X.-H. Li, J.-S. Chen, *Angew. Chem. Int. Ed.* **2015**, *54*, 15165; *Angew. Chem.* **2015,** *127,* 15380.
[20]. L.-B. Lv, T.-N. Ye, L.-H. Gong, K.-X. Wang, J. Su, X.-H. Li, J.-S. Chen, *Chem. Mater.* **2015**, *27*, 544.
[21]. K. Xu, P. Cao, J. R. Heath, *Science* **2010**, *329*, 1188-1191.
[22]. P. Lian, X. Zhu, S. Liang, Z. Li, W. Yang, H. Wang, *Electrochim. Acta.* **2010**, *55*, 3909.
[23]. B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, W. Schnick, *J. Am. Chem. Soc.* **2003**, *125*, 10288.
[24]. X.-H. Li, J.-S. Chen, X. Wang, M. E. Schuster, R. Schlögl, M. Antonietti, *Chemsuschem* **2012**, *5*, 642.
[25]. B. Govinda Rao, P. Sudarsanam, A. Rangaswamy, B. M. Reddy, *Catal. Lett.* **2015**, *145*, 1436.
[26]. N. Li, X. Lang, W. Ma, H. Ji, C. Chen, J. Zhao, *Chem. Commun.* **2013**, *49*, 5034.
[27]. L. Liu, S. Zhang, X. Fu, C.-H. Yan, *Chem. Commun.* **2011**, *47*, 10148.
[28]. Y. Yao, L. Wang, L. Sun, S. Zhu, Z. Huang, Y. Mao, W. Lu, W. Chen, *Chem. Eng. Sci.* **2013**, *101*, 424.
[29]. Y.-Z. Chen, Z. U. Wang, H. Wang, J. Lu, S.-H. Yu, H.-L. Jiang, *J. Am. Chem. Soc.* **2017**, *139*, 2035.
[30]. X.-H. Li, J.-S. Chen, X. Wang, J. Sun, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 8074.
[31]. J. H. Stenlid, T. Brinck, *J. Am. Chem. Soc.* **2017,** *32,* 11012,

Entry for the Table of Contents (Please choose one layout)

Layout 2:

FULL PAPER



Li-Bing Lv,[+] Shi-Ze Yang, [+] Wei-Jie Feng, Wen-Yu Ke, Bing Zhang, Hong-Hui Wang, Juan Su, Xin-Hao Li, and Jie-Sheng Chen**

Page No. – Page No.

Room-temperature activation of molecular oxygen over a metal-free triazine-decorated sp^2-carbon framework for green synthesis

Room-temperature activation of O_2 can be achieved over an atomic-scale carboncatalyst prepared via decorating sp^2-carbon framework with triazine (TA-G) for highly efficient organic synthesis. The TA-G has a Fermi level lied in the middle of the oxygen 2p antibonding orbital of the absorbed O_2 to weaken the O-O bond and thus boost the room-temperature and additive-free activation of oxygen molecules.