Supporting Information

Catalytic Selectivity of Nanorippled Graphene

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Materials and methods

The monolayer graphene powder was commercialized supplied by ACS Material and used directly without further purification. The effective surface area and corresponding pore volumes were measured as \sim 400 m^2/g and $\sim 1.3 \text{ cm}^3/g$, respectively. Its morphology was carefully characterized by field emission scanning electron microscopy (SEM, Zeiss Sigma) at an acceleration voltage of 5 kV. The SEM images before and after catalyzing the $H_2 - O_2$ reaction at 600 °C are shown in Fig. 1a. To provide further morphological information on the constituent graphene flakes, a small amount of the powder was dispersed in plenty of ethanol by mild sonication and then the suspension was drop-casted onto a piece of oxidized Si wafer. Fig. S1a shows an SEM image for the deposited flakes, from which the corresponding statistics (Fig. S1b) on their size distribution estimates the average lateral size of about 1 µm. A few representative and isolated flakes were further characterized by atomic force microscope (AFM, Fastscan from Bruker). As shown in Figs. S1c-e, the typical thickness was < 1 nm, in agreement with the known values for monolayer graphene, which was prepared by a similar reduction of graphene oxide. To characterize the materials' chemical structure, we employed Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). FTIR spectra were recorded on a Bruker TENSOR II FTIR spectrometer. The optical resolution was 1 cm⁻¹ as implemented by using a KBr beam splitter. XPS measurements were performed using an electron analyzer (ESCALAB 250Xi, Thermo Fisher Scientific) and Al K α X-rays (Al K α , hv = 1486.7 eV). To analyze the composition and relative amount of carbon- and oxygen-containing groups/bonds, the XPS C 1s and O 1s spectra were analyzed and fitted by Gaussian–Lorentzian (GL30) functions using the Avantage software.

Experimental setup and notes

We employed a customized setup to investigate the reaction of hydrogen and oxygen catalyzed by the graphene powder. A quartz tube (diameter, 5 mm and length, 30 cm) containing a certain amount of the material was sealed and connected to a larger and stainless-steel gas chamber. The latter was equipped with a pressure gauge so that changes in the gas pressure in the whole assembly can be monitored as a function of time. The setup was first pumped down to a vacuum of $<10^{-5}$ mbar and then filled with a gas mixture containing H₂, O₂ and Ar. The partial pressures of H₂ and O₂ was carefully controlled and the total pressure was 1 bar. To initiate the catalytic reaction and also, measure temperature (*T*) dependences, the quartz tube containing the graphene powder was heated up, leaving the rest of the assembly at room temperature, as illustrated in Fig. S2. This uneven heating led to the observation in Fig. 2a that the pressure measured at 600 °C was only increased by ~10% with respect to that at room *T*, rather than a factor of ~2 as estimated using the ideal gas law and simply assuming *T* = 600 °C. Detailed analysis is provided below.

In this setup, the volume of the annealed quartz tube V_2 only accounted for ~15% of the total volume V_{tot} . At room $T(T_0)$, we have

$$P_0 V_{\rm tot} = n_{\rm tot} R T_0 \tag{1}$$

where P_0 is 1 bar, n_{tot} is the total moles of gas molecules and R is the gas constant.

When the quartz tube was heated to
$$(T_0 + \Delta T)$$
, the gas molecules contained in the tube is described by:

$$(P_0 + \Delta P) V_2 = n_2 R (T_0 + \Delta T)$$
⁽²⁾

with $(P_0 + \Delta P)$ the gas pressure measured for the whole setup and n_2 the number of moles of gases contained in the annealed tube. Smaller amount of molecules resided in the tube due to diffusion to the cold volume. Also, we assume n_{tot} remained the same during the heating stage from T_0 to $T_0 + \Delta T$. For the rest part of the setup with the volume $(V_{\text{tot}} - V_2)$ and at T_0 , we have:

$$(P_0 + \Delta P) (V_{\text{tot}} - V_2) = (n_{\text{tot}} - n_2) RT_0$$
(3)

Combining eqs. (1) to (3), we obtain:

$$\frac{\Delta P}{P_0 + \Delta P} = \frac{\Delta T}{T_0 + \Delta T} \frac{V_2}{V_{tot}}$$
(4)

If we put the known parameters into eq. (4), we would find ΔP is only about 10% that of P_0 , in agreement with our observation in Fig. 2a.

Simulations

The theoretical calculations presented in this paper utilized the density functional theory (DFT) method implemented in the VASP software¹. The exchange-correlation potential and ion-electron interactions were described using the generalized gradient approximation (GGA) and projected augmented wave (PAW) methods^{2,3}. For structural relaxation, a kinetic energy cutoff of 500 eV and a $3\times3\times1$ k-point meshes were employed⁴. The van der Waals interactions were treated by the semi-empirical DFT-D2 method^{5,6}. All atoms were allowed to be fully optimized to the ground state, considering spin-polarization. The lattice constant of graphene was optimized as 2.46 Å. Out-of-plane graphene ripples were created by applying compressive strain on an 8×8 supercell containing 128 carbon atoms. The curvature t/D of a created ripple is characterized by the ratio of its height t to the corrugation diameter D (schematically shown in Fig. S8a). We used climbing-image nudged elastic band (CI-NEB) methods to search for the transition state within seven images between the initial state and the final state⁷⁻¹⁰. In our previous work¹¹, we found the energy barrier for hydrogen dissociation on graphene ripples exhibits a monotonic dependence on their curvature t/D, and higher curvature generally leads to a lower dissociation barrier. To provide a simple description for the underlying physical picture of the observed $H_2 - O_2$ reaction without sacrificing its key features, the curvature of the simulated graphene ripples was set as 12% and the calculated barriers were compared with that of hydrogen dissociation, which was well-established as ~0.6 eV¹¹.

As a first attempt, we calculated the dissociation barrier of an O_2 molecule over the created graphene ripple, to distinguish whether it is H_2 or O_2 that dissociates more easily on nanorippled graphene. As shown in Fig. S7, after trying many different configurations for the final state of dissociated O adatoms being bonded to graphene's surface, we found that all the calculated barriers for O_2 dissociation (1.2-1.9 eV) are much higher than H_2 dissociation (~0.6 eV). This suggests the direct oxidation of graphene is quite difficult with respect to its hydrogenation, and the latter should occur first followed by the reaction of O_2 with the dissociated H adatoms, in agreement with our experiments and analysis.

Bearing this result in mind, we simulated the reduction of O_2 by the H adatoms that were produced by the dissociation of H₂ molecules on the ripple's surface (Fig. S8). Our measurements (Figs. 2-4) suggest that the final products contained hydroxyl groups and were physisorbed on the surface of graphene, resulting in negligible changes in graphene's chemical structure (Fig. 1). Accordingly, two reaction routes were considered in our simulations, with the resulting hydroxyl radicals either physisorbed or chemisorbed on the surface of graphene, as illustrated in Fig. S8a. We found that the barrier for the reaction of O_2 with H adatoms is quite small (~0.2 eV, Fig. S8b), resulting in the formation of hydroxyl radicals that were transiently physisorbed on graphene's surface. Then two hydroxyls could rapidly recombine to form a more energetically favorable (due to the exothermic reaction $2(-OH) \rightarrow H_2O_2$ with a final energy of -1.6 eV, Fig. S8b) and physisorbed H₂O₂ molecule, consistent with our experimental results shown in Figs. 2-4 and analysis described in the main text. Furthermore, the physisorbed H₂O₂ molecule could further dissociate on the surface of nanorippled graphene, resulting in two chemisorbed hydroxyl groups (Fig. S8b). The formation of chemically bonded hydroxyls places in practice as a more energetically stable configuration with respect to the physisorbed H_2O_2 molecule, because the reaction is exothermic with a lower final energy of -3.4 eV (Fig. S8b). However, a notably higher barrier of ~0.9 eV should be overcome, which is much higher than that for the formation of H_2O_2 . These simulations results agree well with our experimental measurements.

Supplementary figures



Fig. S1 (a) SEM image of the graphene flakes within the powder and (b) corresponding size distribution. The powder was first dispersed in ethanol by mild sonication, and then casted onto an oxidized silicon wafer for imaging. Because of the sonication which might cleave larger flakes into smaller ones, the actual lateral size might be larger than that shown in the statistics. (c-e) AFM images of a few representative graphene flakes. Scale bar, 1 μ m; color scale, -2 nm to +2 nm. Insets are height profiles extracted from the AFM scans, indicating the flakes are monolayer.



Fig. S2 Schematic of the experimental setup. V_2 denotes the volume of the annealed quartz tube and V_{tot} is the volume of the whole assembly.



-2.4 nm

Fig. S3 AFM images of pristine graphene monolayers after overnight annealing at 600 °C in (a) 90% $H_2 - 10\% O_2$, (b) 90% Ar $- 10\% O_2$ and (c) 80% Ar $- 20\% O_2$. The graphene crystals were mechanically exfoliated on an oxidized silicon wafer (thickness of SiO₂, ~290 nm). The small white dots in (a, b) are presumably contaminations from the reaction chamber whereas the notably higher roughness and nanoscale pits in (c) are due to oxidation. The sub-nanometer variations in height in (a, b) are caused by the roughness of the underlying SiO₂ substrate. Same color scale (-2.4 nm to +2.4 nm) for (a-c).



Fig. S4 P(t) for thermal cycling of a 95% H₂ – 5% O₂ gas mixture in the absence of graphene powder. The quartz tube was first heated from room T (RT) to 600 °C, then annealed at 600 °C for at least 10 hours and finally cooled down to RT. The three stages are clarified by vertical dashed lines.



Fig. S5 P(t) for thermal cycling of 10 mg graphene powder in the presence of 1 bar pure H₂. Dashed vertical lines separate the three stages: from RT to 600 °C, at 600 °C and from 600 °C to RT.



Fig. S6 P(t) for thermal cycling of a 95% Ar – 5% O₂ gas mixture with 10 mg of graphene powder. Dashed vertical lines separate the three stages: from RT to 600 °C, at 600 °C and from 600 °C to RT.



Fig. S7 Simulations for the dissociation of O_2 on a graphene nanoripple (curvature $t/D \approx 12\%$). (a) Initial state for an oxygen molecule being physisorbed over the constructed graphene ripple. (b-e) Energy profiles for the oxidation of the graphene ripple with the dissociated oxygen atoms being adsorbed on different sites, as indicated in the insets.



Fig. S8 Simulations for the reaction of O_2 with H adatoms on the graphene ripples. (a) Schematics for the proposed reaction routes, leading to the formation of hydroxyl groups either physically or chemically adsorbed. Note that the physisorbed hydroxyl radicals could rapidly recombine into the more stable H_2O_2 molecules. (b) Energy profiles for the proposed reaction routes in (a). Insets are representative snapshots for some of the key states as indicated by the blue points.

References for SI

- 1. G. Kresse and J. Furthmuller, *Comput. Mater. Sci*, 1996, **6**, 15-50.
- 2. P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953-17979.
- 3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 4. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
- 5. T. Kerber, M. Sierka and J. Sauer, J. Comput. Chem., 2008, 29, 2088-2097.
- 6. S. Grimme, J. Comput. Chem., 2006, **27**, 1787-1799.
- 7. D. Sheppard, R. Terrell and G. Henkelman, J. Chem. Phys., 2008, **128**, 134106.
- 8. D. Sheppard, P. H. Xiao, W. Chemelewski, D. D. Johnson and G. Henkelman, *J. Chem. Phys.*, 2012, **136**, 074103.
- 9. G. Henkelman, B. P. Uberuaga and H. Jónsson, J. Chem. Phys., 2000, **113**, 9901-9904.
- 10. D. Sheppard and G. Henkelman, J. Comput. Chem., 2011, **32**, 1769-1771.
- P. Z. Sun, W. Q. Xiong, A. Bera, I. Timokhin, Z. F. Wu, A. Mishchenko, M. C. Sellers, B. L. Liu, H. M. Cheng, E. Janzen, J. H. Edgar, I. V. Grigorieva, S. J. Yuan and A. K. Geim, Proc. Natl. Acad. Sci. U.S.A., 2022, **120**, e2300481120.