

Surface Chemistry for Synthesizing Porous Nanographenes by Transition-Metal-Free Activation of Methane

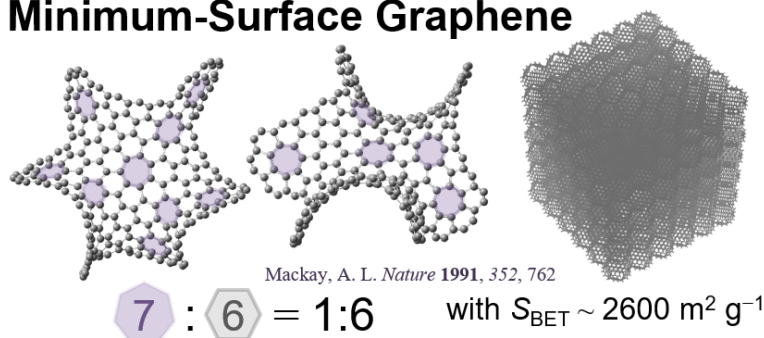
Abstract

The joint team of [Dr. Masanori Yamamoto](#) (Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan), [Dr. Kaoru Yamazaki](#) (Institute for Materials Research, Tohoku University, Japan), and [Dr. Devis Di Tommaso](#) (Queen Mary, University of London, the United Kingdom) revealed a mechanistic understanding of the early-stage activation of CH₄ molecule at the molecular level for synthesizing nanoporous graphene materials, by using experimental and computational chemistry approach. This study showed that the formation of defects by surface engineering is crucial for efficient utilization of CH₄ at lowered temperatures of reactions. These findings will also be of great importance in relation to achieve ideal “Minimum-Surface Graphene” as well as better catalysts for direct methane reforming in future.

Background

Graphene is a carbon material made from planarly arranged hexagons, showing notable physical properties.[1] When pentagons are introduced to the plain, fullerene as a 0-dimensional sphere could be obtained with a positive curvature.[2] When wrapped cylindrically, carbon nanotubes as 1-dimensional materials could be obtained.[3] On the contrary, introduction of heptagons and octagons into the graphene architecture will lead to a negative curvature, and the presence of ordered 3-dimensional graphene materials has been predicted by Mackay and co-workers in 1992.[4] Figure 1 shows the schematic of **Minimum-Surface Graphene**.

Minimum-Surface Graphene



This Work

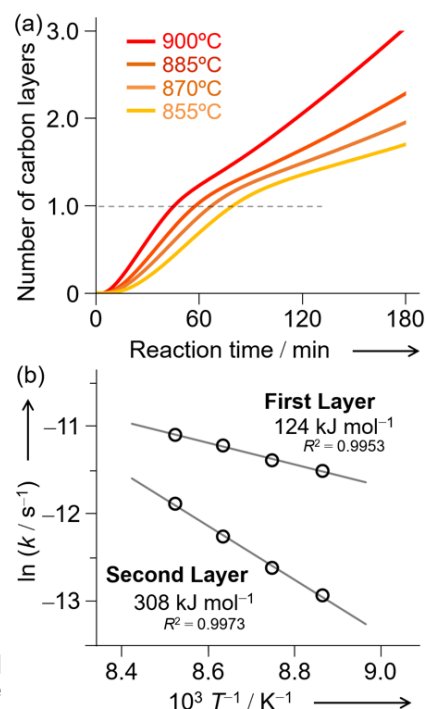
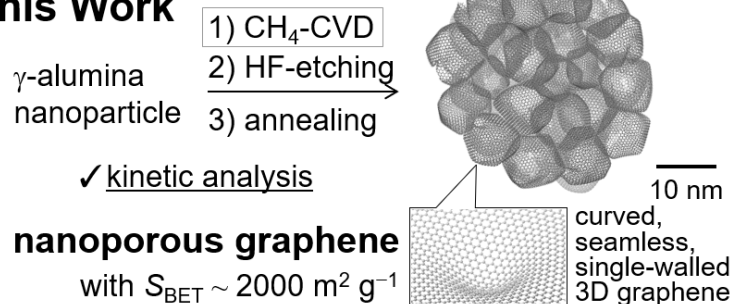


Figure 1. Schematics of 3D graphenes, and kinetic analysis of CH₄ activation on metal oxide nanoparticles.

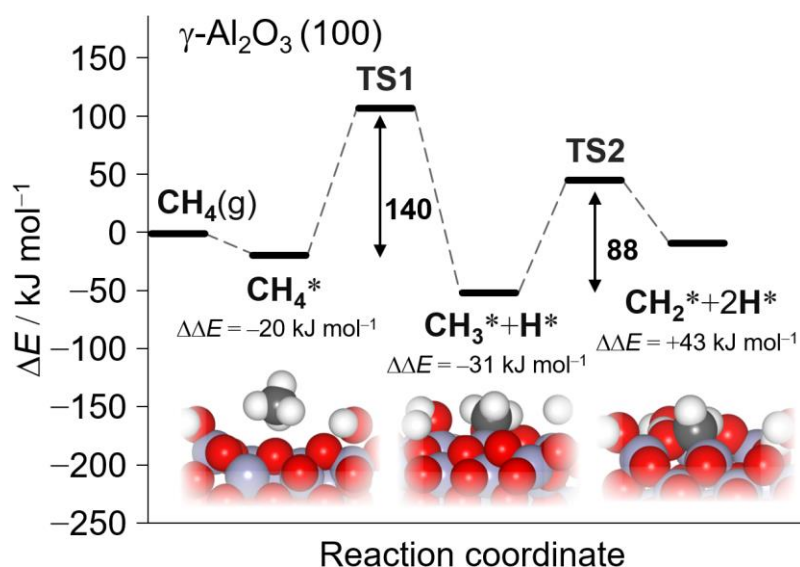
However, the synthesis of such an ideal 3D graphene material has yet to be achieved.

Many research groups have approached to this ideal material, and one of the state-of-the-art material would be zeolite-templated carbon (ZTC): Prof. Takashi Kyotani in Tohoku University reported the synthesis of ZTC by chemical vapor deposition (CVD) of propylene and other hydrocarbons,[5] and ZTC showed an ordered structure of the unit cell with 1.2 nm periodicity as confirmed by XRD, which reflected the ordered structure of the corresponding zeolite template. However, detailed analysis of ZTC including Raman spectroscopy and temperature-programmed desorption of gases showed that ZTC is amorphous carbon with many edge-defects rather than “graphene.” On the contrary, Dr. Takahiro Morishita, Prof. Michio Inagaki, and co-workers reported that the use of MgO as a template of CVD-based carbonization led to high-quality porous graphene materials.[6] Later, we also reported that chemically stable methane (CH_4) would be deposited onto the surfaces of alumina nanoparticles to give high-quality nanoporous graphene (NPG).[7] A structural regularity of ZTC and a high-quality of graphene (NPG) should be achieved at the same time for the synthesis of “minimum surface porous graphene materials,” but currently we have no template materials that can tolerate high-temperature CH_4 -CVD: We recognized that CH_4 -CVD at high temperatures led to the thermal collapse of the structures when many conventional templates were tested. If we reduce the reaction temperature of CH_4 -CVD by enhancing the reaction rate, the synthesis of “minimum surface porous graphene materials” could be ensured using the present template materials available. To this aim, we investigated detailed surface chemistry and kinetics during CH_4 -CVD on alumina nanoparticles, **to elucidate the key factor governing the CH_4 -CVD reaction.**

Findings

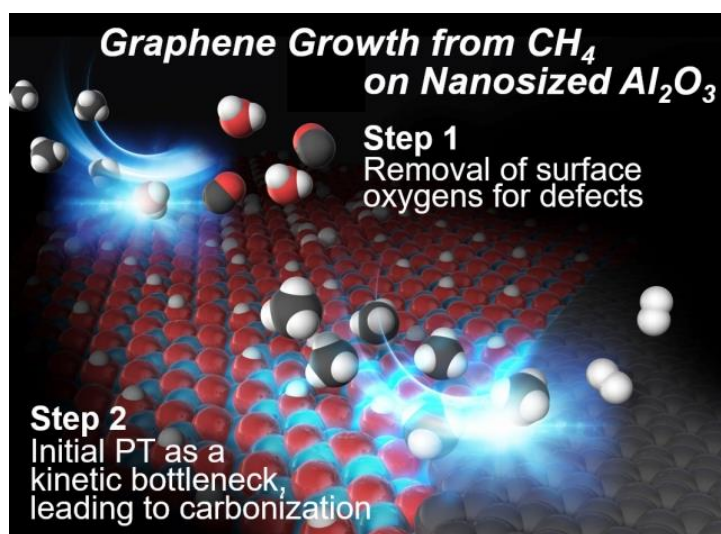
Practically, the kinetic analysis of CH_4 -CVD on γ -alumina nanoparticles at various temperatures (Figure 1a,b) was coupled with computational chemistry using density functional theory (DFT) to elucidate the surface chemistry. As a consequence, we found the followings:

- CH_4 -CVD was initiated at 900°C following the formation of surface oxygen defect by reactions with CH_4 .
- Thus formed surface **defect catalyzes the early-stage CH_4 activation with no use of transition metal reaction center**, and this is supported by both experimental and computational chemistry.
- Kinetic analysis showed that the rate of CH_4 -CVD is pseudo-first order with respect to CH_4 partial pressure, and the apparent activation energy of CH_4 -CVD (E_a^\ddagger) was 124 kJ mol^{-1} for the first-layer deposition (Figure 1b). This value is in a good agreement with an apparent activation energy of the initial dissociative adsorption of CH_4 on a metal oxide surface ($E_a^\ddagger = 120 \text{ kJ mol}^{-1}$) calculated by DFT.



- D) The kinetic analysis indicated that the rate-determining step of the CH₄-CVD is the initial associative adsorption of CH₄, and charge density analysis by DFT calculation suggested that **the rate-determining step is a proton transfer (PT)** from a CH₄ molecule by a conventional Lewis acid/base mechanism[8] rather than radical mechanism.
- E) Sequential PTs from CH₄ on surfaces of metal oxides gave a reactive surface-bound methylene (Al=CH₂*), and its dimerization and subsequent couplings will lead to carbonization on surfaces.
- F) Due to the catalysis of defected surfaces, the carbonization on metal oxide nanoparticles ($E_a^\ddagger = 124 \text{ kJ mol}^{-1}$) is more than 2-times faster than the carbonization of deposited carbon ($E_a^\ddagger = 308 \text{ kJ mol}^{-1}$), and **this kinetically enabled us to synthesize single-walled porous nanographene.**

Thus, activation of methane on alumina nanoparticles was kinetically feasible to give porous nanographene (NPG) materials with no use of transition metal active centers by CH₄-CVD conditions, and the early-stage activation of CH₄ has been supported by both experimental and computational chemistry. This study shows that a surface oxygen defect formed by high-temperature reaction with CH₄ plays a crucial role in CH₄-CVD. Activation of chemically stable CH₄ was initiated by the single proton transfer (PT) step, and the PT from CH₄ is the rate-limiting step of the whole process in CH₄-CVD. **Advanced surface engineering for defects will improved the reactivity to CH₄ and lowering the reaction temperature of CH₄ activation on surfaces of metal oxides, and this will enable us to synthesizing "ideal 3D nanoporous graphenes" by CH₄-CVD using a readily available template having ordered nanoporosity in the future.**



This work has been accepted and published in *Chemical Science*, the flagship journal of the Royal Society of Chemistry (RSC), entitled with “Porous Nanographene Formation on γ -Alumina Nanoparticles via Transition-Metal-Free Methane Activation” (22 February 2022).[9]

Porous Nanographene Formation on γ -Alumina Nanoparticles via Transition-Metal-Free Methane Activation

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Review Comment 1:

“This is a very interesting paper that reports an original and novel investigation of the formation of nanographene on gamma alumina. The work finds convincing evidence that vacancies provide the active sites for the methane decomposition.”

Review Comment 2:

“This is a nice piece of work and I personally found myself enjoying reading it.”

Acknowledgement

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Keywords

Methane activation, direct methane reforming, nanoporous graphene, chemical vapour deposition

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References

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. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163
3. a) S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603–605; b) S. Iijima, T. Ichihashi, Y. Ando, *Nature* **1992**, *356*, 776–778; c) P. M. Ajayan, S. Iijima, *Nature* **1992**, *358*, 23
4. H. Terrones, A. L. Mackay, *Nature* **1991**, *352*, 762–763
5. Z. Ma, T. Kyotani, A. Tomita, *Chem. Commun.* **2000**, 2365–2366
6. a) M. Inagaki, S. Kobayashi, F. Kojin, N. Tanaka, T. Morishita, B. Tryba, *Carbon* **2004**, *42*, 3153–3158; b) T. Morishita, T. Tsumura, M. Toyoda, J. Przepiorski, A. W. Morawski, H. Konno, M. Inagaki, *Carbon* **2010**, *48*, 2690–2707; c) M. Inagaki, M. Toyoda, Y. Soneda, S. Tsujimura, T. Morishita, *Carbon* **2016**, *107*, 448–473
7. M. Yamamoto, S. Goto, R. Tang, Y. Hayasaka, Y. Yoshioka, M. Ito, M. Morooka, H. Nishihara, T. Kyotani, *ACS Appl. Mater. Interfaces* **2021**, *13*, 38613–38622
8. A. Matsuda, H. Tateno, K. Kamata, M. Hara, *Catal. Sci. Technol.* **2021**, *11*, 6987–6998
9. M. Yamamoto, Z. Qi, S. Goto, Y. Gu, T. Toriyama, T. Yamamoto, A. Aziz, R. Crespo-Otero, D. Di Tommaso, M. Tamura, K. Tomishige, T. Kyotani, K. Yamazaki, *Chem. Sci.* **2022**, *13*, 3140–3146