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Featured Letter

Co-synthesis of large-area graphene and syngas via CVD method from greenhouse gases

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ABSTRACT

In this study, we report a novel and efficient way to produce large-area graphene and syngas simultaneously from CH_4 and CO_2 via CVD. The successful synthesis of syngas was confirmed by online gas chromatography characterization whereas the graphene produced within the same process was verified using Raman spectroscopy, Raman mapping and HRTEM. This work helps to better understand graphene growth from CH_4 and CO_2 and improve the CVD method by providing a novel pathway for the synthesis of large-area graphene with a valued by-product. With our derived CVD approach, graphene was grown while producing syngas and consuming green-house gases which is of great importance in this current climate change phenomenon.

1. Introduction

Graphene is virtually transparent since it is a layer of sp^2 carbon based allotrope with thickness of one atom [1,2]. Large-area graphene is a material that can enable hundreds of new applications, from flexible electronics [3–7] to photovoltaic cells [8,9]. As graphene is very thin, it requires a very infinitesimal amount of carbon precursor during a chemical vapor deposition (CVD) reaction. In fact, most of the carbon precursors will be discharged as effluent. However, there has been little emphasis on reducing the effluent discharged from the process or converting the effluents into by-products with economic value. To develop synthesis methods producing high quantity of quality graphene with lower production cost is a subject of intense research and it is still challenging [10,11].

In recent years, the importance of H_2 [12] and O_2 [13] in assisting CVD of graphene have been investigated. Aside from those two, CO_2 has also been used in combination with CH_4 as a mild oxidant to increase the quality of large-area graphene layers produced by in situ etching of low quality graphitic material while removing growing of carbon impurities [14]. Another research group has found that CH_4 with CO_2 can lead to the formation of a sub-oxide layer on Ni, inducing a surface-mediated mechanism instead of the typical bulk-mediated one [15]. A trait did not appear when only CH_4 is utilized during the CVD process. Both CO_2 and CH_4 are greenhouse gases that contribute greatly to climate change. And since they are available abundantly including as biogas from wastewater treatment, their potential as carbon feedstock for graphene growth via CVD would be logical. Syngas is a vital intermediate for the production of acetic acid, ammonia, methanol, hydrogen and other synthetic hydrocarbon fuels. Hence, the conversion of CH_4 and CO_2 (synthetic biogas) into syngas while also producing graphene is a valuable alternative approach. In this study, we investigated the utilization of CO_2 and CH_4 as carbon precursor to synthesize large-area graphene by a one-step ambient pressure CVD while also producing syngas as a by-product. Solving two major problems of graphene cost and greenhouse gases emission in one process.

2. Experimental procedure

The used Ni foil (thickness 125 μm) was purchased from Sigma-Aldrich. It was cut into rectangles of 2 cm x 1 cm. For a CVD reac-

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tion, a rectangle was then bended to a U-shaped structure at the center of its length as illustrated in Fig. 1(a). The Ni substrate was heated up to 900 °C in 10 sccm of H_2 and 10 sccm of N_2 atmosphere. Once the temperature reached 900 °C, the reaction was maintained for 60 min at ambient pressure with 20 sccm of CH_4, 20 sccm CO_2 and 10 sccm N_2 flowing. The experiment was repeated with the same conditions without CO_2. Graphene transfer was performed using wet chemical etching via a nitric acid solution (1.44 M).

The graphene obtained were characterized by using Raman spectroscopy and Raman mapping (with a Renishaw InVia micro-Raman System, 633 nm), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) (with a FEI Tecnai G2 F20 S-TWIN) at 200 kV and online gas chromatography (GC) System 7890A from Agilent Technologies. The first measurement of each effluent composition was taken 15 min after the beginning of the reaction because gaseous flows was unstable beforehand. The syngas production was evaluated by calculating CH_4 and CO_2 conversion into H_2 and CO and the H_2/CO ratio after CVD reaction. The calculations were made by using the following equations (n is gas flowrate):

$$\text{Conversion of } CH_4 : X_{CH_4}(\%) = \frac{n_{CH_4,in} - n_{CH_4,out}}{n_{CH_4,in}} \times 100 \tag{1}$$

$$\text{Conversion of } CO_2 : X_{CO_2}(\%) = \frac{n_{CO_2,in} - n_{CO_2,out}}{n_{CO_2,in}} \times 100 \tag{2}$$

$$\text{Selectivity of } H_2 : S_{H_2} = \frac{n_{H_2,out}}{2\left(n_{CH_4,in} - n_{CH_4,out}\right)} \times 100 \tag{3}$$

$$\text{Selectivity of CO} : S_{CO} = \frac{n_{CO,out}}{\left[\left(n_{CH_4,in} - n_{CH_4,out}\right) + \left(n_{CO_2,in} - n_{CO_2,out}\right)\right]} \times 100 \tag{4}$$

$$\text{Ratio of } H_2/CO = \frac{S_{H_2}}{S_{CO}} \tag{5}$$

3. Results and discussions

The developed U-shaped catalyst creates an aerodynamic current for the inlet flow while also increasing the area of contact between the substrate and the reactants. From Raman spectroscopy analysis of the transferred graphene film, the three primary peaks at $\sim 2680\ cm^{-1}$, $\sim 1580\ cm^{-1}$ and $\sim 1350\ cm^{-1}$ representing the 2D-band, G-band and D-band respectively were observed. Fig. 1(b) illustrates the Raman spectroscopy of the graphene produced simultaneously with syngas in the presence of CO_2. I_{2D}/I_G was calculated to be around 0.547 implying the multilayer nature of the synthesized graphene. Further characterization using Raman mapping I_{2D}/I_G and I_D/I_G clarified that the large-area film produced was a multilayer graphene (MLG) as illustrated in Fig. 1(c) and (d).

Parallel lines were observed by HRTEM in agreement with the multilayer structure of the grown graphene when both CO_2 and CH_4 were present (Fig. 2(a)). The thickness of the MLG was observed to be higher when CO_2 was absent for the CVD synthesis (Fig. 2(c)). In agreement, electron diffraction revealed high-quality lattice arrangement lattice point in Fig. 2(b). The presence of CO_2 alongside CH_4 means that the reaction will closely follows the catalytic CO_2 reforming of methane (CRM) reaction mechanism. The carbon active species for graphene carbon deposition can come from either CH_4 or CO_2 as illustrated in Eqs. (6)–(11). However, CO_2 requires an additional stage to become CO before it can become carbon active species. Moreover, the dehydrogenation of CH_4 is endothermic in nature while CO will go through an exothermic reaction of releasing energy in order to generate carbon active species for graphene synthesis. The overall simultaneous produc-

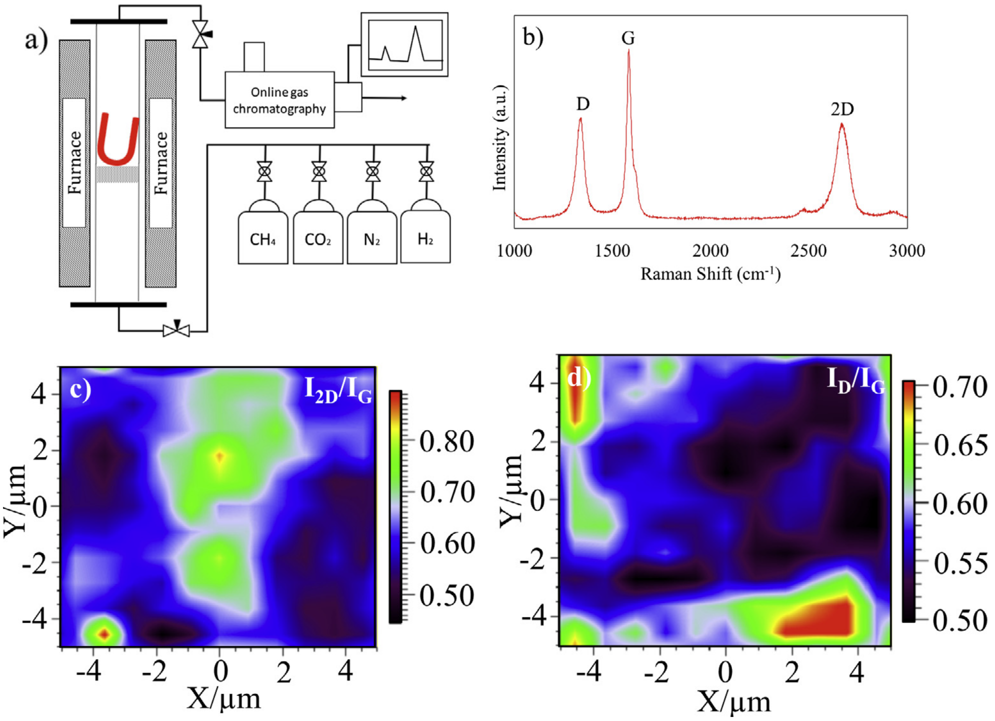

Fig. 1. (a) Scheme of the developed graphene CVD setup. Raman spectroscopy (b) and Raman mapping (c) I_{2D}/I_G and (d) I_D/I_G of the grown multilayer graphene.

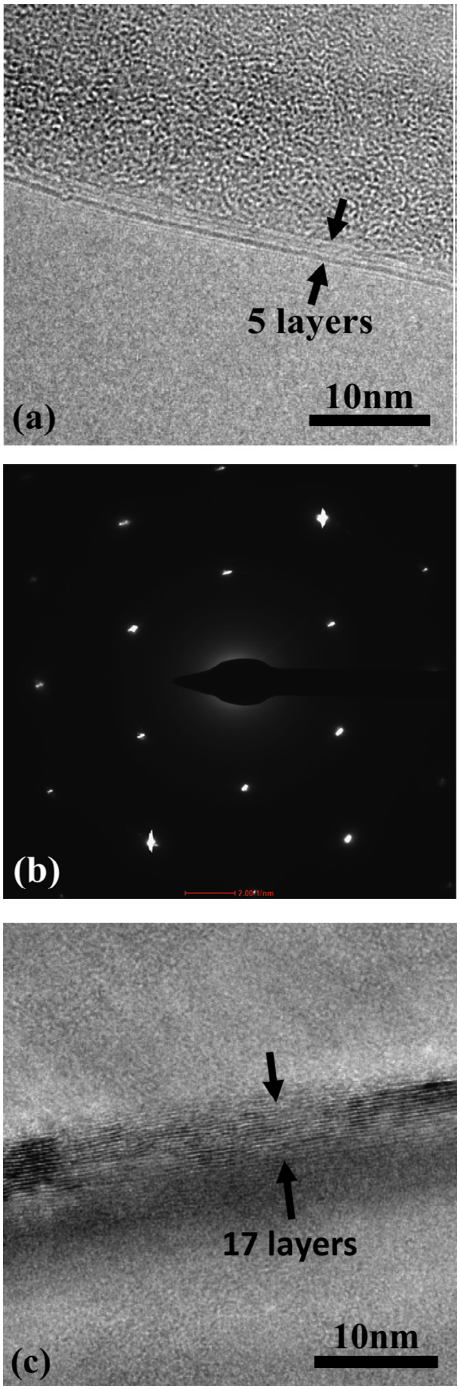

Fig. 2. Typical HRTEM images of graphene edge synthesized from CO_2 and CH_4 (a) and from CH_4 (c), respectively. Electron diffraction of graphene synthesized from CO_2 and CH_4 (b).

tion of syngas is represented by Eq. (6) where CO_2 will mainly supply the CO while CH_4 will supply the H_2 [16].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad H_{298\,K} = 247.3\,kJ/mol \tag{6}$$

$$CH_4 \rightarrow C\cdot + 2H_2 \quad H_{298\,K} = 86.3\,kJ/mol \tag{7}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad H_{298\,K} = 41\,kJ/mol \tag{8}$$

$$2CO \rightarrow C + CO_2 \quad H_{298\,K} = -159.9\,kJ/mol \tag{9}$$

$$CO + H_2 \rightarrow H_2O + C\cdot \quad H_{298\,K} = -131.1\,kJ/mol \tag{10}$$

$$CO \rightleftharpoons C\cdot + CO_2 \quad H_{298\,K} = -173.0\,kJ/mol \tag{11}$$

As shown in Fig. 3(a), the online gas chromatography results show the conversion of CH_4 into H_2 and CO_2 into CO at around 41.73 and 57.77% respectively, obtained by using equation Eqs. (1)–(5). As time progressed, the gas conversion gradually diminishes. There is a simple explanation for the deterioration of gas conversion which is graphene growth have a direct impact on the activity and selectivity of the Ni catalyst. Carbon deposition or coking is considered as a key problem for CRM. However, by controlling the parameters we were able to synthesize graphene simultaneously with syngas. This is the first time that syngas has been produced simultaneously with good quality graphene within a 1 step process. One important thing to note is the average ratio of H_2 to CO is around 0.7:1.0 or 70.7%. Based on this observation, we concluded that the conversion of CH_4 into H_2 was lower than that of CO_2 into CO. Ideally, the ratio of the two needs to be 1 to 1 so that the yield of syngas can be maximized. In order to attain a better ratio of syngas, H_2 can be added post-reaction or the quantity of CH_4 needs to be higher by a factor of 1.44 from its original flow which will be discussed in future studies. The low conversion level of the reactants has a lot to do with the shape of the metal catalyst. Flat metal catalyst has less direct area of contact with the reactant gaseous. Fig. 3(b)–(d) demonstrates the raw online GC data as an example. A schematic presentation of the plausible mechanism of the reaction was illustrated in Fig. 3(e). CH_4 will supply most of the carbon active species for graphene growth as it only requires dehydrogenation process in order for it to become carbon active species. CO_2 requires 2 steps before it can become a fully fledge building block for graphene growth. Moreover, CO_2 will also act as a mild etchant in the graphene growth mechanism and removes carbon of lesser quality from depositing on the metal substrate while also thinning the layers of graphene in the process [14,15]. The success of co-synthesizing graphene and syngas has open up the possibility for further exploration of using similar setup specifically the feasibility of using actual biogas as a precursor for graphene growth which will be reported in future research.

4. Conclusions

In summary, large-area graphene and syngas were successfully synthesized simultaneously by the ambient pressure CVD method by using greenhouse gases in the form of CO_2 and CH_4 as carbon sources. The mixture of CO_2 and CH_4 was designed to mimic synthetic biogas composition which means that biogas can be a viable carbon source for graphene synthesis. We have shown that a continuous multilayer graphene film with good quality was produced. CO_2 was evidenced to play the double role of precursor and mild oxidant for the removal of carbon layers of lesser quality. This is a novel and simple method for fabricating graphene that could open up a novel route for by-products co-synthesis while also utilizing greenhouse gases in a one-step process.

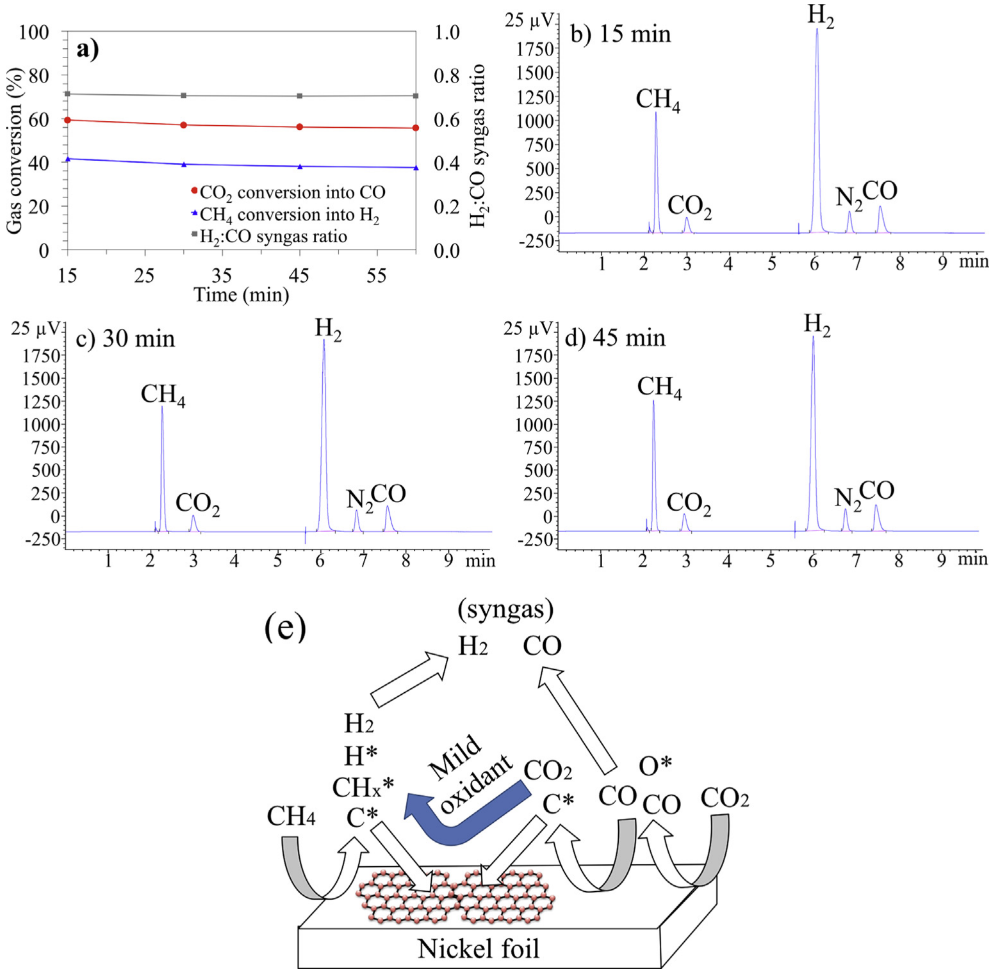

Fig. 3. (a) Gas conversion of CH_4 to H_2 and CO_2 to CO over CVD at 900 °C for 60 min and the ratio of H_2:CO produced. Raw online GC results at 15 min (b), 30 min (c) and 45 min (d) for CVD from CO_2 and CH_4. (e) Schematic representation of the graphene and syngas co-synthesis CVD mechanism.

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References

[1] X.S. Li, Y.W. Zhu, W.W. Cai, M. Borysiak, B.Y. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, Nano Lett. 9 (2009) 4359–4363.
[2] J. Jang, M. Son, S. Chung, K. Kim, C. Cho, B.H. Lee, M. Ham, Sci. Rep. 5 (2015) 17955.
[3] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. Il Song, Y.-J. Kim, K.S. Kim, B. Özyilmaz, J.-H. Ahn, B.H. Hong, S. Iijima, Nat. Nanotechnol. 5 (2010) 574–578.
[4] W. Yang, C. Wang, J. Mater. Chem. C. 4 (2016) 7193–7207.
[5] S. Sharma, G. Kalita, R. Hirano, S.M. Shinde, R. Papon, Carbon N. Y. 72 (2014) 66–73.
[6] N. Salehifar, J.S. Shayeh, S.O. Ranaei Siadat, K. Niknam, A. Ehsani, S. Kazemi Movahhed, RSC Adv. 5 (2015) 96130–96137.
[7] J. Shabani Shayeh, A. Ehsani, M.R. Ganjali, P. Norouzi, B. Jaleh, Appl. Surf. Sci. 353 (2015) 594–599.
[8] L. Kuhn, N.E. Gorji, Mater. Lett. 171 (2016) 323–326.
[9] Y. Zhang, L. Zhang, C. Zhou, Acc. Chem. Res. 46 (2013) 2329–2339.
[10] R. Kumar, R.K. Singh, D.P. Singh, Renew. Sustain. Energy Rev. 58 (2016) 976–1006.
[11] J. Sun, Y. Chen, M.K. Priydarshi, Z. Chen, A. Bachmatiuk, Z. Zou, Z. Chen, X. Song, Y. Gao, M.H. Rummeli, Y. Zhang, Z. Liu, Nano Lett. 15 (2015) 5846–5854.
[12] J. Liu, S.P. Adusumilli, J.J. Condoluci, A.C. Rastogi, W.E. Bernier, W.E. Jones, Mater. Lett. 153 (2015) 132–135.
[13] S. Yin, X. Zhang, C. Xu, Y. Wang, Y. Wang, P. Li, H. Sun, M. Wang, Y. Xia, C. Te Lin, P. Zhao, H. Wang, Mater. Lett. 215 (2018) 259–262.
[14] A.J. Strudwick, N.E. Weber, M.G. Schwab, M. Kettner, R.T. Weitz, J.R. Wu, K. Mu, ACS Nano. 9 (2015) 31–42.
[15] I.H. Son, H.J. Song, S. Kwon, A. Bachmatiuk, S.J. Lee, A. Benayad, J.H. Park, J. Choi, H. Chang, M.H. Ru, ACS Nano. 8 (2014) 9224–9232.
[16] M. Khavarian, S. Chai, A. Rahman, Fuel. 158 (2015) 129–138.