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Waste to Value Added Products: Graphene

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Abstract: *Globally, approximately 2 billion tons of solid waste is generated annually, of which 34-53% is composed of biodegradable organic materials (Abad et al. 2019). Organic fractions of municipal solid wastes (OFMSW); It consists of waste from food production, household residues from food preparation, leftovers, expired food, waste from restaurants and food outlets. While more than 100 billion tons of resources are transferred to the economy every year, more than 60% of them are waste and result in an increase in greenhouse gas emissions, which is one of the triggers of the climate crisis. EU; to improve sustainability in solid waste management, it has promoted some directives (1999/31/EC) to reduce production, encourage recycling, encourage resource selection and reduce biodegradable waste sent to landfill. The EU's aim for 2050 is to be the carbon neutral first continent, and in this direction, it plans all its policies under the name of "Green Deal". The Green Deal describes a framework that includes emission reduction, circular economy, zero pollution, transformation of agriculture and rural areas, sustainable transport, energy transition and financing all of these. In this context, the circular economy plays an important role in providing a conceptual way to minimize environmental impact and maximize resource (energy and material) recovery from solid waste. The anaerobic digestion (AD) process metabolizes the OFMSW to energy-rich biomethane and carbon dioxide by several microbial steps. The intermediates of AD can be transformed into value-added products, such as biofuels, biogas, bioethanol, etc. This review presents alternative value-added products such as "graphene" using biomethane from biogas by anaerobically digested OFMSW. This will close the loop of the life cycle of OFSMW via attaining a sustainable circular economy with a product with higher added value than biomethane. With this respect, the separation route of biomethane in transforming OFSMW into value-added products and graphene production techniques from biomethane are briefly assessed.*

Keywords: *Sustainability, circular economy, biogas, waste, graphene*

1. Introduction

Today, the use of renewable energy resources (biomass, hydraulic, wind, solar, geothermal, etc.) that can be an alternative to fossil fuels for combating global warming, closing the energy gap, solving environmental problems and sustainable development is gradually increasing.

Population growth and economic development cause serious increases in the amount of domestic organic solid waste all over the world. The problems associated with solid waste disposal and its negative environmental effects necessitate correct waste management(Balbay, Sarıhan, and Avşar 2021). With the management of organic wastes, which constitute a large part of domestic waste, it is possible to provide common benefits for both the environment and the economy by ensuring waste disposal, recycling and reuse (Ariunbaatar et al. 2014). In most of the developing countries, methods such as landfill, dumping, incineration and compost are chosen for domestic solid waste disposal (Braguglia et al. 2018). These methods pose serious hazards due to various reasons such as unsuitable land conditions for storage in urban areas, mixing of leachate into groundwater, and

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release of greenhouse gases and other polluting gases into the environment (Ahmed et al. 2021). In addition to these, the continuous increase in energy demand increases the interest of local governments in the environmental dimension of these wastes as well as in the issue of energy recovery from organic fractionated wastes. Since biogas production, especially from organic wastes by anaerobic processes, is included in the scope of renewable energy, it is considered among the disposal methods that provide both economic and environmental benefits (Panwar, Kaushik, and Kothari 2011).

Vegetable, agricultural, animal waste and food industry wastes are biomass sources, which is one of the renewable energy sources. The use of these wastes as an energy conversion system brings solutions to environmental problems, while organic fertilizers with high energy and nutritional value are obtained from organic wastes. With these systems, In addition to preventing waste of resources, wastes are recycled in order to reduce the negative effects of emerging energy crises. Microbiological evaluation of wastes containing organic matter is important in terms of both preventing environmental pollution and providing clean energy production. Biogas is predominantly (60-80%) methane and carbon dioxide gas, which is formed as a result of the biodegradation of organic materials under anaerobic conditions. The conversion of various organic substances to CH4 and CO2 is carried out by the mixed microbiological flora (Anukam et al. 2019). With anaerobic treatment, energy equivalent to 2700 kW-h can be produced by removing 1000 kg of COD. 90-98% of the organic carbon removed in anaerobic digestion is converted to biogas (methane).

Anaerobic digestion takes place in four successive stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Adekunle and Okolie 2015). Figure 1 shows a simplified flow of its four stages.

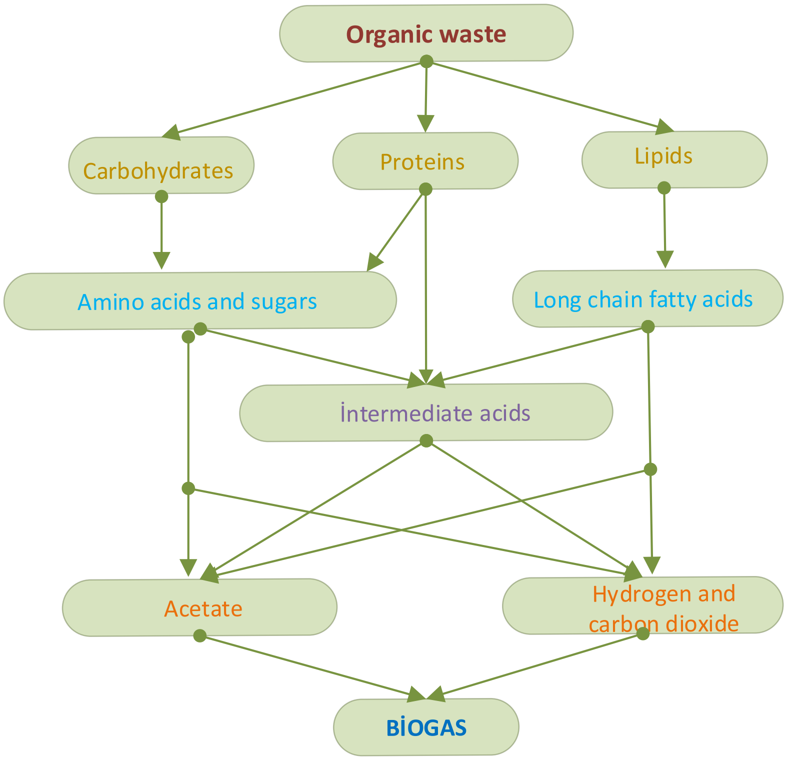

Fig. 1. Schematic diagram of biogas production

In the hydrolysis stage; long-chain organic molecules are broken down by acidogenic bacteria and converted into organic acids, and hydrogen and carbon dioxide gases are released during the process (Li, Park, and Zhu 2011). In the acidogenesis stage; hydrolysis products are fermented or oxidized anaerobically. Sugars and amino acids are converted to VFAs (mainly acetate, propionate, butyrate), hydrogen (H2), CO2 and ammonia (lactate and alcohols can also be produced) through fermentative reactions, in which organic compounds act as both electron donors and acceptors (Córdova and Chamy 2020). At the stage of acetogenesis; Long chain fatty acids and volatile fatty acids produced during the acidogenesis stage are converted to acetate, CO2 and H2 by acetic acid producing (acetogenic) bacteria. Volatile fatty acids and long chain fatty acids act as electron donors in these reactions. The electron acceptor for these reactions is hydrogen (Hassaan et al. 2022). In order for the reactions to proceed in the direction of the products thermodynamically, the hydrogen concentration in the environment must be low. Bacteria that produce methane using hydrogen, on the other hand, control the hydrogen concentration in the environment by using H2 as an electron donor and CO2 as an electron acceptor. Finally, methanogenesis is achieved as a result of the broken of acetic acid from the previous stages in anaerobic digestion or the synthesis of H2 and CO2 (Vincent, Jennerjahn, and Ramasamy 2021). Approximately 30% of the methane produced in anaerobic reactors consists of H2 and CO2, and 70% consists of the breakdown of acetic acid (Capodaglio and Bolognesi 2019). Archaea that produce methane from H2 and CO2 reproduce much faster than archaea that use acetic acid. Therefore, if there is sufficient H2 and CO2 in the environment, CH4 production continues in this way. In fact, this step is a critical step in all anaerobic digestion, despite being the slowest biochemical reaction. Different bacterial groups are active at all stages.

The intermediates of AD can be transformed into value-added products, such as biofuels, biogas, bioethanol, etc. This review presents alternative value-added products such as “graphene” using biomethane from biogas by anaerobically digested OFMSW. To the best of our knowledge, no previous reviews have provided a complete picture of the different higher value-added products beyond biogas from AD so far. Therefore, this review concisely reviews how to obtain a high value-added product such as graphene via biomethane produced from AD.

1.1. Biogas Conversion and Upgrade

The main components of biogas are CH4 and CO2, average percentage these gasses are waves in the range of 50-70% and 30-50% at proper running AD systems, respectively. Main energy carrier at the biogas is CH4. Conventionally, biogas turns into heat and heat-electricity both in site. For this conversion burning systems used for heat production, this excess heat can be used for heating greenhouses, factories and working areas. At combine heat and power (CHP) systems biogas turns into electricity and heat, electricity can be feed to grid and heat can be used for heating the digester and further heating demands at house or facilities (Makaruk, Miltner, and Harasek 2010).

Addition to CH4 and CO2 biogas also contains N2, CO, O2, H2, H2S, siloxanes, hydrocarbons (alcohols, VFA, terpenes) etc. in pretty low concentrations. Considering its availability and energy potential, the most important gas emerges as CH4 in biogas. Because of that CH4 should be enriched to contribute its usability. In general biogas purification consists of two main steps, first is biogas cleaning and second one is biogas upgrading. At the first step harmful and toxic substances like H2S, CO, siloxanes, VOCs, and NH3 are removed, then at second step biogas is enriched in the term of CH4 content, basically by removing the CO2. The main aim of second step is convert the gas to fuel standards in the term of calorific value. The main processes for biogas purification are; water scrubbing, amine scrubbing, membrane separation, pressure swing adsorption and cryogenic separation. These processes have advantages and disadvantages compared to each other. For instance, cryogenic processes have very high purification level however have very high energy consumption, membrane processes have high purification level however have high initial investment and operational cost, water scrubbing does not have very high purification levels but have simplicity and low costs. (Atelge et al. 2020). Biogas purification is essential if it will have used for further like using at vehicles, pumping to local gas pipeline, methanol and ethanol production etc. Additionally, separation of CO2 from biogas also provides opportunity to further usage of CO2.

1.2. Is it possible another option?

Anaerobic digestion (AD) is a natural process in which organic materials are converted to biogas by fermentative bacteria and methanogens. The intermediates of AD can be transformed into value-added products, such as biofuels, biogas, bioethanol as in explained the upper section. Generally, AD is used to produce biogas (contained biomethane) by waste materials from landfills, farms, or wastewater treatment plant digesters, and then biomethane is converted to electricity or heat by power engines. Additionally, digestate as one of the end-product of AD can use in the production and recovery of higher-value biochemicals beyond biomethane, such as volatile fatty acids, lactic acid, and Polyhydroxyalkanoates (PHAs) etc. (Lü et al. 2021). Specific methods are available including valuable compounds to obtain from digestate via thermal conversion or extraction technologies. On the other hands, these applications have several difficulties such as operational drawbacks and energy costs. However, biogas up-grade technologies have been researched for relatively many years and have successful industrial-scale applications. Therefore, it may be more advantageous to conduct research on alternative products with high added value to be obtained from biogas.

Looking into the technological developments, it is seen that recent research efforts were majorly focused on graphene-based material usage at numerous industrial fields sensors, energy storage materials, treatment technologies, solar cells, medicine, and many other applications (Ghaffarkhah et al. 2022). As is known, graphene is a carbon-based material and is produced using commercially available fossil-sourced methane. It may be possible to use biogas for graphene production after removing impurities (CO2 and water vapor, etc.) other than biomethane. In line with this approach, a greener approach will be introduced in the production of graphene as a new generation material and biomethane which is a significant cost in graphene synthesis could be more economically supplied from organic waste material such as OFMSW, agricultural or industrial waste (Figure 1). Thus, biomethane sourced graphene can be a significant milestone in decarbonizing the graphene production industry. According to our knowledge, there is no publication about discussion of the usage of biomethane to produce graphene. Therefore, lab and pilot scale experiments and cost-benefit analysis are needed to verify the possibility of industrial production of biomethane based-graphene.

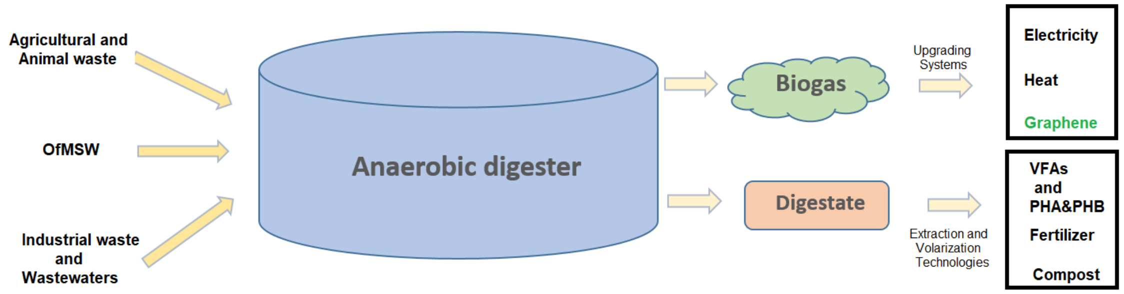

Fig. 2 Waste to value-added products

1.3. What is the Graphene?

Graphene, single layer of graphite, is one of the most researched allotropes of carbon. Graphene has high electrical and thermal conductivity, high transparency, high surface area and mechanical durability. Thanks to its almost perfect physical, chemical, electronic, optical, and photonic properties, graphene has a wide range of applications from energy field to sensor technology and from electronic applications to photonic ones. There are various techniques for the graphene synthesis such as mechanical exfoliation, epitaxial growth, chemical exfoliation, and chemical vapor deposition (CVD) techniques, and each technique has its own advantages (Wang et al. 2009). CVD is one of the best-known and commonly employed method for 2D material synthesis in particular for graphene. This method provides homogeneous and low-cost synthesis of graphene in large area [2]. The CVD method is basically one of the bottom-up material synthesis approach. The CVD mechanism regarding graphene synthesis is based on the decomposition of hydrocarbon gases at elevated temperature and the diffusion of carbon atoms onto a metal surface.

There are many hydrocarbon sources such as methane (CH4), acetylene (C2H2) and benzene (C6H6), are brought into contact with the metal substrates like Ni, Cu, Ru, Ir, Co and Pd at high temperature in a CVD chamber that kept at low pressure (Muñoz and Gómez-Aleixandre 2013). Many parameters are essential for the synthesis of large scale of graphene with low defect density by the CVD method. The temperature stability, the purity of the hydrocarbon gas sources, gas flow rate (H2/CxHx), the annealing time, the growth time, growth pressure, the cooling rate and purity of the metal substrates has crucial role for the graphene synthesis (Mattevi, Kim, and Chhowalla 2011). The CVD process generally consists of four sections: heating, annealing, growth and cooling (Fig 3).

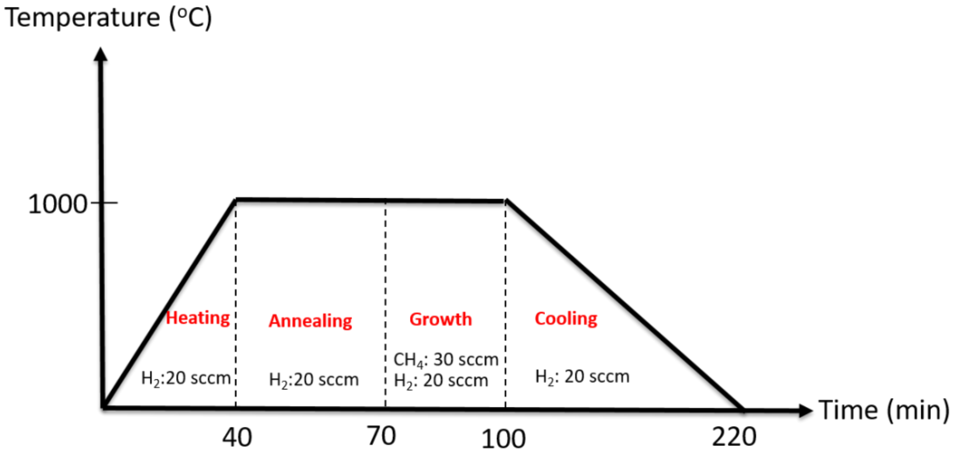

Fig. 3. Typical temperature profile and flow rate for the growth of graphene on copper surface using methane

CVD approaches have different processes like atmospheric-pressure chemical vapor deposition (APCVD), low-pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD), or plasma-assisted chemical vapor deposition (PACVD), and laser-enhanced chemical vapor deposition (LECVD). Besides hybrid processes combining features of both physical and CVD have also emerged. LPCVD has important place between these processes. LPCVD provides 2D material synthesis with high homogeneity and quality. This widely employed CVD approach for synthesizing commercial graphene films can also employ in graphene synthesis using biomethane produced in AD. Thus, it could be possible to synthesize graphene more economically using biomethane produced via a sustainable source as OfMSW through AD process. There are several studies focused on the production of graphene by pyrolysis and various carbonization techniques (Safian, Haron, and Mohamad Ibrahim 2020), no integrated study aimed at biogas production with the AD process and graphene production from biogas was found in the literature.

2. Conclusion

AD is a widely applied and established technology for the treatment of organic waste or wastewater. In this review, it is highlighted that amount of OFSMW generation, anaerobic digestion of OFSMW, biogas upgrading systems, valuable products of coming from AD. Additionally, this review presents alternative value-added products such as “graphene” using biomethane from biogas by anaerobically digested OFMSW as a new generation material. This will close the loop of the life cycle of OFSMW via attaining a sustainable circular economy with a product with higher added value than biomethane. According to our knowledge, this is the first review about discussion of the usage of biomethane to produce graphene from OFSMW.

3. Acknowledgement

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References

[1] Abad, Vanessa, Romina Avila, Teresa Vicent, and Xavier Font. 2019. "Bioresource Technology Promoting Circular Economy in the Surroundings of an Organic Fraction of Municipal Solid Waste Anaerobic Digestion Treatment Plant : Biogas Production Impact and Economic Factors." Bioresource Technology 283(March):10–17. doi: 10.1016/j.biortech.2019.03.064.

[2] Adekunle, Kayode Feyisetan, and Jude Awele Okolie. 2015. "A Review of Biochemical Process of Anaerobic Digestion." Advances in Bioscience and Biotechnology 06(03):205–12. doi: 10.4236/abb.2015.63020.

[3] Ahmed, Banafsha, Vinay Kumar Tyagi, Kaoutar Aboudi, Azmat Naseem, Carlos José Álvarez-Gallego, Luis Alberto Fernández-Güelfo, A. A. Kazmi, and Luis Isidoro Romero-García. 2021. "Thermally Enhanced Solubilization and Anaerobic Digestion of Organic Fraction of Municipal Solid Waste." Chemosphere 282:131136. doi: 10.1016/J.CHEMOSPHERE.2021.131136.

[4] Anukam, Anthony, Ali Mohammadi, Muhammad Naqvi, and Karin Granström. 2019. "Processes A Review of the Chemistry of Anaerobic Digestion: Methods of Accelerating and Optimizing Process Efficiency." doi: 10.3390/pr7080504.

[5] Ariunbaatar, Javkhlan, Antonio Panico, Giovanni Esposito, Francesco Pirozzi, and Piet N. L. Lens. 2014. "Pretreatment Methods to Enhance Anaerobic Digestion of Organic Solid Waste." Applied Energy 123:143–56. doi: 10.1016/j.apenergy.2014.02.035.

[6] Atelge, M. R., A. E. Atabani, J. Rajesh Banu, David Krisa, M. Kaya, Cigdem Eskicioglu, Gopalakrishnan Kumar, Changsoo Lee, Y. Yildiz, S. Unalan, R. Mohanasundaram, and F. Duman. 2020. "A Critical Review of Pretreatment Technologies to Enhance Anaerobic Digestion and Energy Recovery." Fuel 270:117494. doi: 10.1016/j.fuel.2020.117494.

[7] Balbay, Şenay, Adem Sarıhan, and Edip Avşar. 2021. "Dünya ' Da ve Türkiye ' de ' Döngüsel Ekonomi / Endüstriyel Sürdürülebilirlik ' Yaklaşımı ' Circular Economy / Industrial Sustainability ' Approach in the World and in Turkey." (27):557–69. doi: 10.31590/ejosat.971172.

[8] Braguglia, Camilla M., Agata Gallipoli, Andrea Gianico, and Pamela Pagliaccia. 2018. "Bioresource Technology Anaerobic Bioconversion of Food Waste into Energy : A Critical Review." Bioresource Technology 248:37–56. doi: 10.1016/j.biortech.2017.06.145.

[9] Capodaglio, Andrea G., and Silvia Bolognesi. 2019. "Ecofuel Feedstocks and Their Prospects." Advances in Eco-Fuels for a Sustainable Environment 15–51. doi: 10.1016/B978-0-08-102728-8.00002-4.

[10] Córdova, Olivia, and Rolando Chamy. 2020. "Microalgae to Biogas: Microbiological Communities Involved." Microalgae Cultivation for Biofuels Production 227–49. doi: 10.1016/B978-0-12-817536-1.00015-1.

[11] Ghaffarkhah, Ahmadreza, Ehsan Hosseini, Milad Kamkar, Ali Akbari Sehat, Sara Dordanihaghighi, Ahmad Allahbakhsh, Colin van der Kuur, and Mohammad Arjmand. 2022. "Synthesis, Applications, and Prospects of Graphene Quantum Dots: A Comprehensive Review." Small 18(2):1–48. doi: 10.1002/smll.202102683.

[12] Hassaan, Mohamed A., Marwa R. Elkatory, Ahmed El Nemr, and Antonio Pantaleo. 2022. "Eco-Friendly Biogas Production from Algal Biomass." Handbook of Algal Biofuels 225–49. doi: 10.1016/B978-0-12-823764-9.00023-6.

[13] Li, Yebo, Stephen Y. Park, and Jiying Zhu. 2011. "Solid-State Anaerobic Digestion for Methane Production from Organic Waste." Renewable and Sustainable Energy Reviews 15(1):821–26. doi: 10.1016/j.rser.2010.07.042.

[14] Lü, Fan, Zhijie Wang, Hua Zhang, Liming Shao, and Pinjing He. 2021. "Anaerobic Digestion of Organic Waste: Recovery of Value-Added and Inhibitory Compounds from Liquid Fraction of Digestate." Bioresource Technology 333(April):125196. doi: 10.1016/j.biortech.2021.125196.

[15] Makaruk, A., M. Miltner, and M. Harasek. 2010. “Membrane Biogas Upgrading Processes for the Production of Natural Gas Substitute.” Separation and Purification Technology 74(1):83–92. doi: 10.1016/j.seppur.2010.05.010.

[16] Mattevi, Cecilia, Hokwon Kim, and Manish Chhowalla. 2011. “A Review of Chemical Vapour Deposition of Graphene on Copper.” Journal of Materials Chemistry 21(10):3324–34.

https://doi.org/10.1039/C0JM02126A

[17] Muñoz, Roberto, and Cristina Gómez-Aleixandre. 2013. “Review of CVD Synthesis of Graphene.” Chemical Vapor Deposition 19(10–12):297–322.

https://doi.org/10.1002/cvde.201300051

[18] Panwar, N. L., S. C. Kaushik, and Surendra Kothari. 2011. “Role of Renewable Energy Sources in Environmental Protection: A Review.” Renewable and Sustainable Energy Reviews 15(3):1513–24.

https://doi.org/10.1016/j.rser.2010.11.037

[19] Safian, Muhammad Taqi-udeen, Umirah Syafiqah Haron, and Mohamad Nasir Mohamad Ibrahim. 2020. “A Review on Bio-Based Graphene Derived from Biomass Wastes.” BioResources 15(4):9756–85.

https://doi.org/10.15376/biores.15.4.Safian

[20] Vincent, Salom Gnana Thanga, Tim Jennerjahn, and Kumarasamy Ramasamy. 2021. “Environmental Variables and Factors Regulating Microbial Structure and Functions.” Microbial Communities in Coastal Sediments 79–117. doi: 10.1016/B978-0-12-815165-5.00003-0.

[21] Wang, By Xianbao, Haijun You, Fangming Liu, Mingjian Li, Li Wan, Shaoqing Li, Qin Li, Yang Xu, Rong Tian, and Ziyong Yu. 2009. “Large-Scale Synthesis of Few-Layered Graphene Using CVD **.” 53–56. doi: 10.1002/cvde.200806737