

# Local Thermochemical Mechanisms in Direct Solar Graphite Synthesis from Methane

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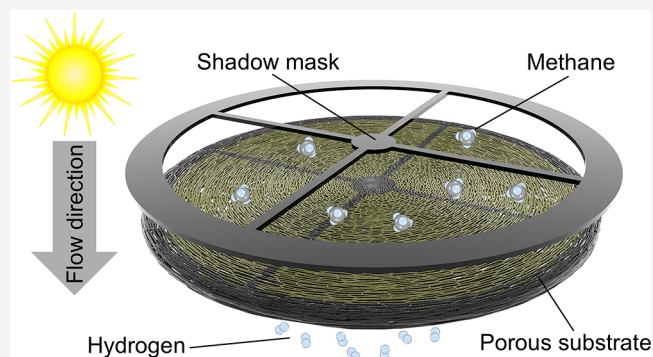


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Supporting Information

**ABSTRACT:** Methane pyrolysis is known to produce hydrogen and solid carbon in a variety of thermal processes. However, the generated carbon product typically belongs to a low-value amorphous type. Here, we elucidate the thermochemical mechanisms of a reaction that produces high-quality graphite via direct solar methane pyrolysis on a porous substrate. By comparing graphite deposition rates and local reaction zone temperatures of exposed and shadowed regions from the same experiment, we clarify the effects of thermolysis and photolysis in this emission-free process that both decarbonizes a fuel and produces a critical material for the sustainable energy transition.



Graphite is a critical material for energy storage in the clean energy transition, and with the increasing demand for lithium-ion batteries and the scarcity of natural graphite, producing clean, high-quality synthetic graphite at high rates is essential to modernizing supply chains in the clean energy economy.<sup>1</sup> Industrial furnaces are widely used in industry for pyrolytic graphitization of petroleum needle coke by heat treatments above 2600 °C and 2–4 kWh of energy per kg of graphite produced in thermal processes that require days or weeks.<sup>2</sup> Aside from the possibility that the supply of such feedstocks derives from pollutive petrochemical refinery processes, the large time and energy required and limited supply of source materials for synthetic graphitization hinders the likelihood that these processes can become both sustainable and scalable. In contrast, here, we elucidate thermochemical details of a process<sup>3,4</sup> that employs simulated solar irradiation to provide exceptionally fast deposition rates of high-quality graphitic carbon.

Exposure to light is a popular approach to facilitate chemical reactions through the possibly synergistic combination of thermochemical and photochemical effects, particularly through the use of photocatalysts.<sup>5</sup> For example, hot charge carriers generated through the decay of localized surface plasmon resonance (LSPR) can induce localized heating at active catalyst sites to produce high reaction rates under moderate conditions.<sup>6</sup> Numerous materials exhibit photo-thermal enhancement, such as metal nanostructures,<sup>7</sup> semiconductors,<sup>8</sup> and carbon-based nanomaterials.<sup>9,10</sup> Unraveling thermal and non-thermal contributions in such chemical reactions has been a persistently challenging topic of research and debate.<sup>11–14</sup>

This communication seeks to examine potential contributions of photolytic effects in direct solar decomposition of methane into high-quality graphite and hydrogen that was reported recently.<sup>3,4</sup> Specifically, we have devised an experiment in which neighboring deposition sites are shadowed and directly exposed through the use of a shadow mask (Figure S2 of the Supporting Information), thus revealing abrupt differences in reaction rates as indicated by the spatial distribution of graphite deposition. The graphical abstract above provides a schematic overview of the experiment, while details of the experimental setup are provided in the Supporting Information. Methane pyrolysis is conducted with a shadow mask under a peak irradiance of 3365 suns, flow rate of 100 standard cubic centimeters per minute (sccm), pressure of 3.33 kPa, and duration of 25 min. The shadow mask is mounted in the front of the fibrous porous carbon substrate (C100, Fuel Cell Earth) under direct irradiation (Figure S1 of the Supporting Information) to create distinct shadowed and exposed regions on the substrate.

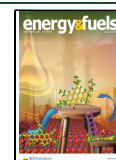
The process creates a unique form of graphite that conformally coats the original carbon fibers such that the graphene layers take a cylindrical form, as shown in Figure 1a, that is highly graphitic, as indicated in the Raman spectra of Figure S5 of the Supporting Information. A pronounced

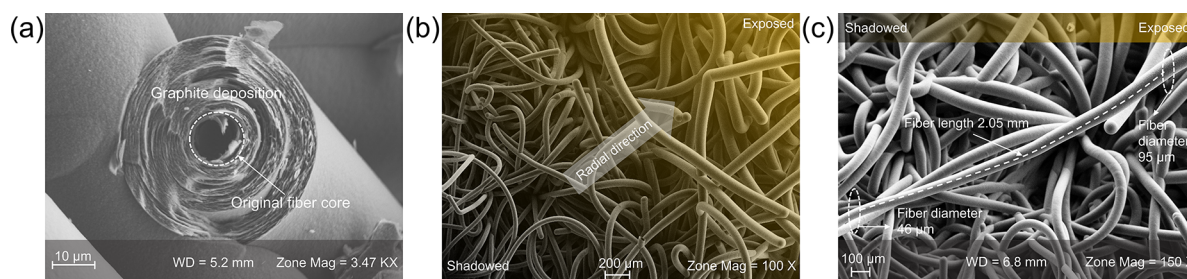
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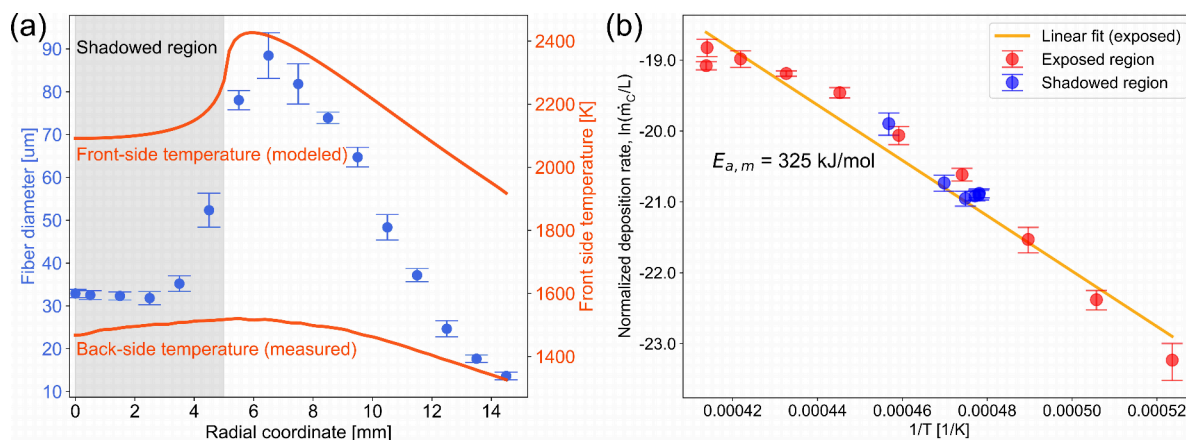
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**Figure 1.** SEM images of conformally deposited graphite: (a) fracture cross section showing cylindrical graphene layering, (b) fibers at the transition from shadowed to exposed regions, and (c) 2 mm long single fiber bridging shadowed and exposed regions from left to right, illustrating the substantially higher growth rate in the exposed region.



**Figure 2.** (a) Radial variation of the fiber diameter and substrate temperatures in the shadowed and exposed regions. Uncertainty ranges correspond to twice the standard deviations of up to five measurements at a given radius. (b) Arrhenius plot of the normalized deposition rate as a function of the modeled inverse front-side temperature with activation energy fitting for the exposed region (red circles). The results for the shadowed region are shown as blue circles.

shadowing effect is apparent in the scanning electron microscopy (SEM) images of panels b and c of Figure 1, in which the fiber diameters increase markedly from the shadowed to exposed regions. To understand the reason for such changes, we measured the back (non-illuminated) side substrate temperature with an infrared camera during deposition, as shown in Figure S3a of the Supporting Information and the lower temperature curve of Figure 2a. Given the extreme thermal environment of the experiment, these were the only direct temperature measurements available, and the relatively flat temperature profile in the central region in moving from the shadowed to the exposed regions initially suggested that the pronounced difference in the graphite fiber diameter (Figure 2a) was caused by a direct photolysis effect.

To assess the possibility of direct photolytic effects, we proceeded to model the front-side (light-facing) substrate temperature based on the measured back-side temperatures and multimode heat transfer mechanisms in fibrous porous substrates (Figure S4 of the Supporting Information). The predicted front-side temperature distribution shown in Figure 2a reveals a large temperature variation from the shadowed to exposed regions, unlike the back-side temperatures. Armed with this temperature model in the primary reaction zone, we created an Arrhenius plot in Figure 2b to assess the reaction's first-order activation energy based on the temperatures and deposition in the exposed region, resulting in a mean activation energy of  $E_{a,m} = 325$  kJ/mol (the activation energy corresponding to the upper and lower limits of the normalized

deposition rate are 316 and 336 kJ/mol) that falls in the expected range for thermal decomposition of methane.<sup>15</sup>

Moreover, when the deposition–temperature data from the shadowed region are superposed on the Arrhenius plot (blue circles in Figure 2b), they fall near the fitting line, suggesting an ordinary thermal decomposition process that does not involve significant non-thermal photolytic effects. These results highlight the critical importance of obtaining local temperature values at reaction sites to distinguish between thermal and non-thermal effects in reactions driven by direct illumination. Had we simply used the back-side temperatures that were directly measured, the conclusion about the effects of direct photolysis would have been misguided.

In conclusion, we have implemented an experiment that allows for the evaluation of solar-driven methane pyrolysis with simultaneously shadowed and directly exposed regions of reaction. We find that accurate representation of the local temperature in the reaction zone is crucial to reaching appropriate conclusions about thermal and non-thermal effects. Future studies should endeavor to implement such temperature measurements in such challenging thermochemical environments. An improved understanding of this phenomenon would greatly aid the optimization and scaling of this method of solar graphite production for the growing battery and clean energy industries.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c03327>.

Experimental details, analytical thermal and chemical models, and supplementary characterization of graphitic products (PDF)

Additional data for Figure 2a, Figure S3, and Figure S5 (XLSX)

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### Notes

The authors declare the following competing financial interest(s): Timothy S. Fisher and R. Mitchell Spearrin are co-founders of SolGraph, Inc., a company specializing in solar-thermal material synthesis. This submitted work is an independent academic study and is not associated with commercial endeavors or intended as a promotion. The other authors have no competing interests to disclose.

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