## KINETICS OF GRAPHENE OXIDE THERMAL DECOMPOSITION IN THE PRESENCE OF CARBON SUBOXIDE

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The thermal reduction of graphene oxide (GO) is an efficient and simple route to prepare graphene-based materials in large quantities. However, this synthesis method has several drawbacks, including a complex mechanism of GO thermal decomposition, a high release of energy, and the formation of structural defects during the process of thermal exfoliation [1, 2]. According to the literature, the thermal reduction of GO could be more precisely controlled using reducing agents, salts, organic dyes or acids [3, 4]. Carbon suboxide ( $C_3O_2$ ) that forms from the reaction between malonic acid and phosphorus pentoxide is a promising additive in the thermal reduction of GO because it decomposes to elemental carbon and carbon monoxide [5]. The supplemental source of carbon could more effectively repair the disordered structure of the reduced GO that could also improve the electronic properties of the final product and ensure the successful application of reduced GO in electrochemical devices.

In this study, we present the impact of  $C_3O_2$  on the kinetics of GO thermal reduction reaction. The GO synthesis was carried out via the modified Hummers' method [6]. Afterwards, the synthesised GO and the prepared homogenous mixture of GO, malonic acid, and phosphorus pentoxide were analysed by using thermogravimetry (TG), derivative thermogravimetry (DTG), and differential scanning colorimetry (DSC) methods at three different heating rates: 2.5 °C min<sup>-1</sup>, 5 °C min<sup>-1</sup>, and 10 °C min<sup>-1</sup>. The kinetic (*E<sub>a</sub>*, *n*) and thermodynamic ( $\Delta H$ ) parameters of the thermal decomposition reaction of GO with and without C<sub>3</sub>O<sub>2</sub> were determined by using Borchardt-Daniels, Kissinger, and Ozawa models [7].

DSC results revealed that the reduction temperature of GO is reduced (up to 125 °C) by using C<sub>3</sub>O<sub>2</sub>. Moreover, it was observed that C<sub>3</sub>O<sub>2</sub> lowers the enthalpy  $\Delta H$  and activation energy  $E_a$  but does not influence the reaction order *n* of GO thermal decomposition. The apparent reaction order *n* for both studied samples was determined to be 0.7. In fact, the mechanism of this process could be modelled including consecutive zero-order and first-order stages. The zero-order process may originate when the energy consumed in the thermal decomposition reaction comes through the basal graphene plane; then, the reaction rate should not depend on the reagent concentration (i.e., the concentration of oxygen functionalities). The first-order process may occur when the energy is absorbed directly by a functional group; this time the reaction rate depends only on the concentration of the reagent. The same reaction order for GO with and without C<sub>3</sub>O<sub>2</sub> reduction reveals the same mechanism for both processes.

## References

- 1. Y. Qiu, F. Guo, R. Hurt, I. Külaots. Carbon 72 (2014) 215-223.
- 2. G. T. T. Le, J. Manyam, P. Opaprakasit, N. Chanlek, N. Grisdanurak, P. Sreearunothai. Diam. Relat. Mater. 89 (2018) 246–256.
- 3. Y. Qiu, F. Collin, R. Hurt, I. Külaots. Carbon 96 (2016) 20-28.
- 4. J. Barkauskas, J. Gaidukevič, G. Niaura. Carbon Lett. 1 (2021) 3.
- 5. M. Allen. Nature **354** (1991) 272.
- 6. X. Yan, J. Chen, J. Yang, Q. Xue, P. Miele. ACS Appl. Mater. Interfaces. 2 (2010) 2521–2529.
- 7. M. V. Alonso, M. Oliet, J.M. Pérez, F. Rodríguez, J. Echeverría. Thermochim. Acta. 419 (2004) 161-167.