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Single Layer Graphene Film by Ethanol Chemical Vapor Deposition: Highly Efficient Growth and Clean Transfer Method

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The choice of ethanol (C₂H₅OH) as carbon source in the Chemical Vapor Deposition (CVD) of graphene on copper foils can be considered as an attractive alternative among the commonly used hydrocarbons, such as methane (CH₄) [1]. Ethanol, a safe, low cost and easy handling liquid precursor, offers fast and efficient growth kinetics with the synthesis of fully-formed graphene films in just few seconds [2]. In previous studies of graphene growth from ethanol, various research groups explored temperature ranges lower than 1000 °C, usually reported for methane-assisted CVD. In particular, the 650–850 °C and 900 °C ranges were investigated, respectively for 5 and 30 min growth time [3, 4]. Recently, our group reported the growth of highly-crystalline, few-layer graphene by ethanol-CVD in hydrogen flow (1–100 sccm) at high temperatures (1000–1070 °C) using growth times typical of CH₄-assisted synthesis (10–30 min) [5]. Furthermore, a synthesis time between 20 and 60 s in the same conditions was explored too. In such fast growth we demonstrated that fully-formed graphene films can be grown by exposing copper foils to a low partial pressure of ethanol (up to 2 Pa) in just 20 s [6] and we proposed that the rapid growth is related to an increase of the Cu catalyst efficiency due weak oxidizing nature of ethanol. Thus, the employment of such liquid precursor, in small concentrations, together with a reduced time of growth and very low pressure leads to highly efficient graphene synthesis. By this way, the complete coverage of a copper catalyst surface with high spatial uniformity can be obtained in a considerably lower time than when using methane.

For most applications and characterizations, after the growth process the graphene films need to be transferred onto arbitrary substrates [7]. Transfer is still a critical process for CVD graphene, capable of impairing graphene quality and the development of reliable and clean means of transfer are still being investigated. Our group first reported on the use of an organic compound, cyclododecane, as a temporary resist to assist the transfer: it can be spin coated on graphene, it is hydrophobic and after assisting the wet etching of the copper catalyst, it sublimates at ambient conditions leaving no residues [8]. It can also considered an eco-friendly process since it does not require the use of solvents for its removal and it can be in principle recovered after transfer process.

In the present work, we explored the formation of a graphene film onto a copper surface by using ethanol, focusing on a rapid synthesis method leading to highly efficient growth process. To this purpose, temperature, growth time and hydrogen flow were kept constant at suitable values, as inferred from previous works, while decreasing the ethanol partial pressure and the total pressure.

Graphene was grown using a CVD system made of a quartz tube furnace where the samples can be rapidly inserted and extracted from the hot zone. Quick syntheses, down to 20 s were performed at different pressures (1 and 6 torr) and at the temperature of 1000°C, under an hydrogen flow of 100 sccm. Ethanol vapor, diluted in Argon (1/200), was let to flow inside the quartz tube. After the CVD process, the films were transferred onto Si/SiO₂ (300nm) by using a cyclododecane resist during the copper etching in Ammonium Persulphate (PSA) [8].

The transferred films were characterized by Raman Spectroscopy. Figure 1 shows the Raman spectra of the samples grown for 20 s (Fig. 1 a, c) and 60 s (Fig. 1 b, d) at 1000 °C and for a hydrogen flow varying between 0 sccm (Fig. 1 c, d) and 100 sccm (Fig. 1 a, b). The main features are the G peak centered at $\sim 1584\text{ cm}^{-1}$, 2D peak at $\sim 2700\text{ cm}^{-1}$ and D at $\sim 1350\text{ cm}^{-1}$. I_D/I_G and I_G/I_{2D} intensity ratios provide information about film defectiveness and thickness respectively. In our previous studies, lower values of I_D/I_G were obtained for longer growth times, indicating higher quality graphene [5] and, although the films appeared completely formed in just 20 s, shorter growths were always more defective. Concerning the thickness, the I_G/I_{2D} ratios indicated the presence of fewer layers at 20 s than at 60 s. The addition of hydrogen (100 sccm) was always observed to improve the I_D/I_G ratio. Conditions for the rapid growth of less defective films were then investigated by reducing the ethanol flow from 20 to 5 sccm and the growth pressure down to 1 torr, and a continuous film was still observed to grow. In Fig.1 (e) the Raman spectra show the positive effect of pressure and precursor reduction, which lead to a barely defective single layer graphene film.

Overall, in this work we have demonstrated that the growth of graphene from ethanol-CVD is very efficient. High quality single layer graphene films can be grown when exposing copper surfaces to ethanol partial pressure as low as 0.2Pa for a handful of second. Finally, we confirmed that the use of cyclododecane support material can ensure clean, sustainable processing of CVD-graphene.

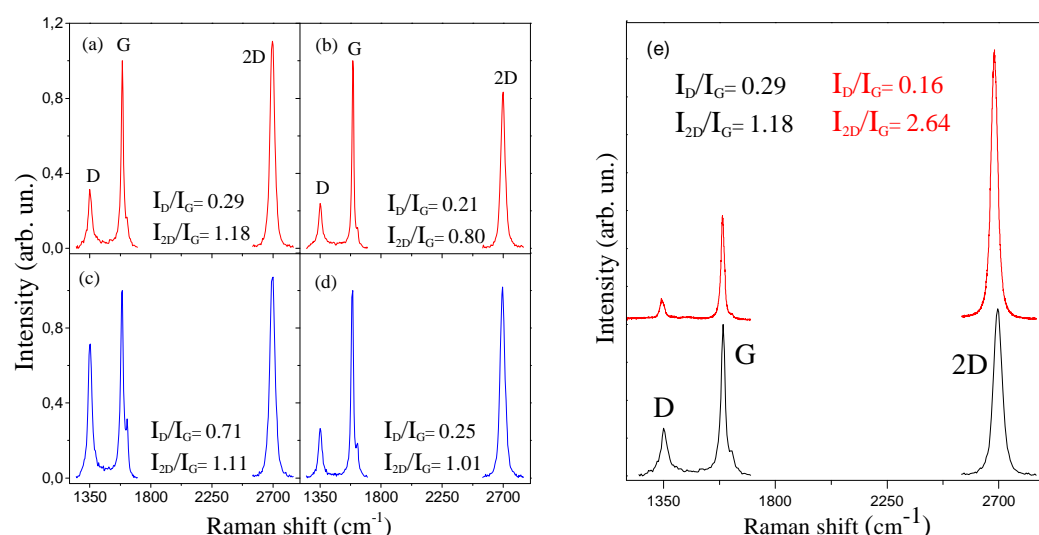


Figure 1: Raman spectra of graphene films grown at 1000°C for 20 s (a, c) and 60 s (b, d) and with hydrogen flow varying between 0 sccm (c, d) and 100 sccm (a, b). Panel (e) shows the Raman spectra of graphene films grown at different ethanol dilution and pressure: 20 sccm and 6 torr (black line), 5 sccm and 1 torr (red line).

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