ELSEVIER

Scalable production of graphene via wet chemistry: progress and challenges

Yu Lin Zhong*, Zhiming Tian, George P. Simon and Dan Li*

Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia

Although enormous scientific progress has been made in the application of graphene and its related materials, the cost-effective and scalable production of graphene still holds the key to its commercialization. If this aspect cannot be successfully addressed, it may eventually struggle for widespread use, such as has occurred for its allotrope, the carbon nanotubes. Ease of graphene production is especially important if it is to be used in bulk applications such as energy storage in automobiles where the large scale and low cost production of the active materials is required. Fortunately, graphene can be produced not only from a cheap and abundant source (graphite), but also can be produced using a variety of low cost methods. This focus review article will examine three promising, scalable methods of graphene production, namely the graphite oxide, liquid-phase exfoliation (LPE) and electrochemical routes, with focus on their recent progress and remaining challenges. The perspective on these routes will be mainly taken from the industrial viewpoint, thus highlighting the pressing issues for graphene commercialization. Some of the main concerns regarding the quality or crystallinity of the graphene sheet produced from such methods and the importance of a comprehensive evaluation of the final bulk graphene materials will also be discussed.

Introduction

The most crucial factor for any material to be commercially viable for industrial scale application is its cost-effectiveness. Currently, platinum may exhibit the highest performance for electrocatalysis and tin-doped indium oxide may display the highest conductivity and transparency, but their low abundance and costs will always fuel the search for a cheaper alternative [1]. In comparison, the large available amount of carbon has ensured its continued usage because the dawn of mankind and has exponentially increased with the discovery of the nanocarbon allotropes. This is especially true for two-dimensional graphene which not only exhibits incredible electronics properties [2] but also many outstanding mechanical properties which are highly sought after by a broad spectrum of applications ranging from ultrafast electronics to mechanical actuators [3,4]. More importantly, there are currently numerous ways to produce graphene (Fig. 1) [5] such that one can always identify a well-suited graphene production method for each and every application [6]. For example, the chemical vapour deposition (CVD) [7–11] and epitaxial growth [12–15] methods are ideal for the fabrication of flexible transparent electrodes and graphene electronics that capitalize on the transparency and high electron mobility of pristine single layer graphene, respectively. However, these production methods might face difficulties in growing or forming graphene materials with porous network structures for increased permeability and bulk surface area. On the other end of the spectrum, there are potentially scalable and low cost methods available to mass produce graphene for applications such as conductive ink or energy storage. However, it is especially crucial that in these applications, graphene must not only outperform, but also cost less than existing materials such as carbon black and activated carbon, to motivate the industries to adopt the new material.

The key for graphene commercialization lies in its production method which essentially determines its cost-effectiveness.

*Corresponding authors:. Zhong, Y.L. (yu.zhong@monash.edu), Li, D. (dan.li2@monash.edu)

1369-7021/ http://dx.doi.org/10.1016/j.mattod.2014.08.019

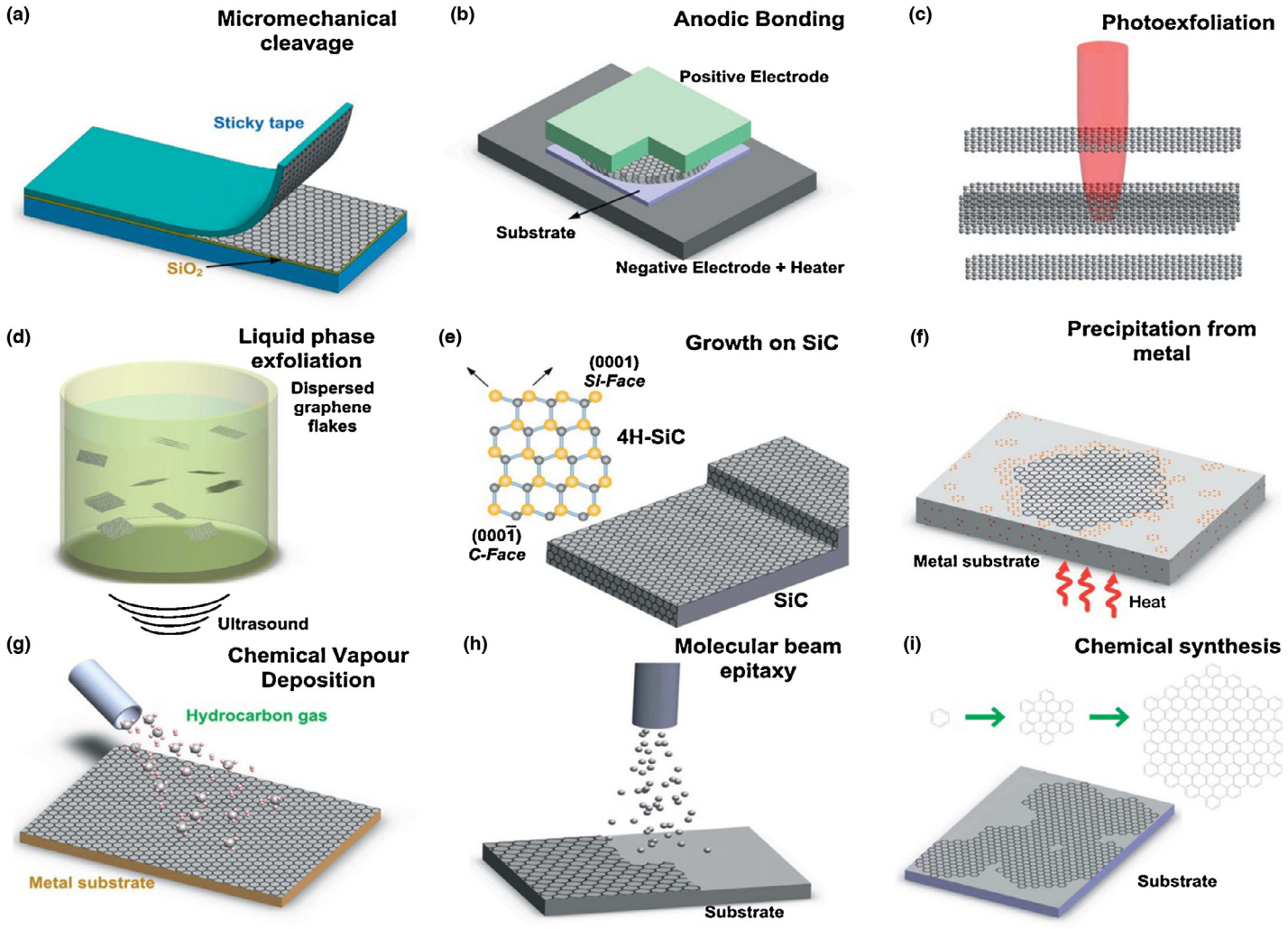

FIGURE 1

Schematic illustration of the main graphene production techniques. (a) Micromechanical cleavage. (b) Anodic bonding. (c) Photoexfoliation. (d) Liquid-phase exfoliation. (e) Growth on SiC. Gold and grey spheres represent Si and C atoms, respectively. At elevated T, Si atoms evaporate (arrows), leaving a carbon-rich surface that forms graphene sheets. (f) Segregation/precipitation from carbon containing metal substrate. (g) Chemical vapour deposition. (h) Molecular beam epitaxy. (i) Chemical synthesis using benzene as building block. Reproduced from Ref. [5] with permission from the Elsevier.

In terms of mass production of graphene, the main factors are the production cost, scalability, reproducibility, processability and the quality of the graphene products. Considering the low cost and abundance of graphite flakes, the wet chemical approaches in exfoliation of graphite to graphene seem to fit all the requirements, except that there is question on the quality of graphene. However, we should take note that the definition on the quality of graphene or rather the efficacy of graphene is highly dependent on its application. For electrocatalysis and storage of capacitive charges, it has been shown that the graphene edges are more superior compared to the graphene basal planes [16] and this is probably due to the localization of HOMO and LUMO levels at the graphene edges [17]. For application as carbocatalysts in the oxidative coupling of organic molecules, it is the edge defects in porous graphene that are responsible for high catalytic activities [18]. Hence, keeping those key factors in mind, this focus review will examine three promising wet chemical graphite exfoliation routes (graphite oxide, liquid-phase exfoliation (LPE) and electrochemical) and highlighting their recent progress and challenges.

Graphite oxide route

The graphite oxide route is currently the most popular wet chemical method to produce graphene materials, namely graphene oxide (GO) [19] and reduced graphene oxide (rGO) [20], based on the enormous amount of research activities employing it. This is due to its potential scalability, high yield and most importantly, its excellent dispersibility in various solvents [21–25] which facilitates processability towards many applications. The main exfoliation mechanism lies in the oxidative intercalation and production of oxygen-containing functional groups on the graphene layers which helps the dispersion and stabilization of GO sheet in water. It is also due to the oxygen-containing functional groups that extended coupling and functionalization chemistry can be applied and helped to propel the use of graphite oxide route. The formation of graphite oxide can be traced back to 1859 when Brodie oxidized graphite in the presence of potassium chlorate and fuming nitric acid [26] and it slowly evolved to the widely used Hummers method that uses a combination of sodium nitrate, potassium permanganate and sulfuric acid [27]. Over the years, efforts have been made to improve on the Hummers method by eliminating the use of sodium