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Preparation of an aqueous graphitic ink for thermal drop-on-demand inkjet printing

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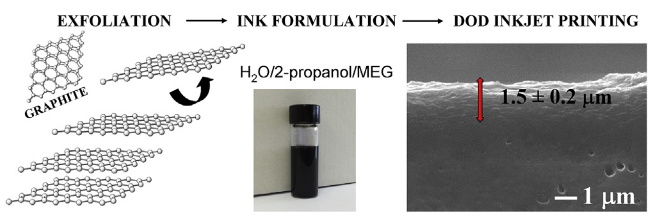
HIGHLIGHTS

- A non-hazardous graphitic ink for thermal DOD inkjet printing was developed.
- The ternary mixture water/ethylene glycol/2-propanol is suitable as solvent.
- Physical properties important for jetting is tailored by solvent composition.
- Surfactant-aided grinding gives exfoliation of graphite without inflicting microstrain.

GRAPHICAL ABSTRACT



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ABSTRACT

A graphitic ink for thermal DOD inkjet printing was developed. Challenges to be met were related to the small size of the getting nozzle (20 μm), demanding high dispersion stability of submicron particles, as well as to the physical requirements of the printer. In addition, solvents potentially hazardous to human health were excluded *a priori*. These necessities led to the development of a ternary aqueous solvent system based on 2-propanol and monoethylene glycol, offering an environmental-friendly alternative to conventional graphene solvents. In addition, high flexibility in terms of physical properties (e.g. surface tension, viscosity, density) important for jetting is obtained. Size reduction and exfoliation, accomplished by wet-grinding of graphite in the presence of a surfactant, were followed by laser diffraction and XRD line broadening analyses, respectively. The separated graphitic colloids used for preparation of inks were composed of ca 30 layers of AB–stacked graphene flakes, as determined by line broadening analyses (XRD data). Jetting of an ink with a solid content of 0.3 mg/mL gave a thickness increase of ca. 25 nm/pass, as determined by FESEM. Electrical characterization evidenced the need to remove residual organic molecules to regain the electrical properties of the graphitic particles.

1. Introduction

Drop-on-demand (DOD) inkjet printing is a computer-controlled technique for non-contact deposition of small drops of fluid/suspension, generated when required. Drops are formed and ejected towards the surface as a result of a pressure pulse in the fluid held behind the printing nozzle. Generally speaking, the pressure pulse is generated either thermally or by direct mechanical actuating using a piezoelectric transducer.

Factors influencing jettability and droplet stability are droplet

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velocity (ν), the physical properties of the ink, i.e. density (ρ), viscosity (η) and surface tension (γ), as well as the diameter of the jetting nozzle (L) [1,2]. Constants obtained from relationships between these parameters, such as the Z-number (Eq. (1)) and the Weber number (Eq. (2)) are used to predict printing quality [1,2]:

$$Z = \sqrt{\frac{\rho \gamma L}{\eta}} \tag{1}$$

$$Weber = \frac{\rho L v^2}{\gamma} \tag{2}$$

Stable drop formation is achieved when the Z-number is in the range 1–10 [1]. According to Hill et al., the Weber number, which takes into account inertial forces of the droplets, also needs to be considered [1].

The diameter of the jetting nozzle is particularly important when the ink is a suspension rather than a solution. To avoid clogging of the nozzle, Lejeuene stated that the ratio between the nozzle diameter and the volume distribution value (D(90)) should be at least 50:1 [3].

Although the main commercial application still remains graphics printing, major research have been performed in inkjet deposition of functional materials for advanced applications such as organic thin-film transistors, light-emitting diodes, solar cells, electronics, memory devices, sensors and biological tasks [4]. Consulting the scientific literature, it appears that piezoelectric DOD is preferred over thermal DOD for inkjet deposition of inorganic material and conductive polymers [5,6]. The popularity of piezoelectric DOD is possibly related to its high versatility regarding the ink. In fact, drop size and velocity can be tailored for a given fluid by changing the actuation pulse [2].

Formulation of conductive inks based on carbon materials, such as carbon nanotubes and graphene, and their subsequent deposition using inkjet technology have been extensively studied [7–9]. Inkjet printing of inks based on Pt-bearing carbon black has been used in polymer electrolyte fuel cell applications [10]. Graphene is a layer of sp2 bonded carbon atoms arranged in a hexagonal lattice, and is the two-dimensional building block of other carbon allotropes (e.g. graphite, carbon nanotubes). Ordered stacking of 2D graphene layers leads to multilayer graphene or 3D graphite whereas a rolled-up graphene sheet forms a single-wall carbon nanotube.

Wet chemical exfoliation techniques are considered promising for cost-effective production of graphene [11]. These include the so-called graphite oxide (GO) route and the liquid phase exfoliation (LPE) route [11]. In the former, graphite is converted to graphite oxide and subsequently exfoliated in a liquid medium, thus yielding graphene oxide. In the final step, reduction to graphene is accomplished. The LPE route generally includes exfoliation of graphite by sonication in a suitable solvent [11], generally high-boiling point organic solvents such as *N*-methyl-2-pyrrolidone (NMP) with Hansen solubility parameters close to those of graphene [12]. Another LPE technique which has shown to be promising is ball-milling of graphitic material for extended periods in organic solvents using exfoliating agents [13,14].

The advantages of using graphene oxide as intermediate phase are related to easier preparation of stable dispersions with high solid load in various solvents which are rather difficult to obtain with pristine graphite obtained by LPE methods. Hence, processability in many applications such as digital printing is facilitated. In fact, the most common method to obtain graphene films through inkjet printing technology is to deposit graphene oxide which is reduced in a post-deposition step by thermal or chemical treatment [15–17]. Major drawbacks are the product quality, which is degraded due to the presence of structural defects and residual oxygen [18], and the need for an additional post-deposition reduction step, motivating continuous search for improvements of LPE methods. Particularly referring to inkjet printing applications, some of these improvements include the exchange of high-boiling point solvents such as *N*-methyl-2-pyrrolidone (NMP), often used for both exfoliation and ink formulations [19], with environmental-friendly solvents through tailoring of the Hansen solubility parameters [9] or by using surface-active polymers [20–23] or covalent functionalization of the graphene surface [20]. This mirrors a general trend in LPE and subsequent preparation of stable graphene dispersions [11,24,25]. For example, Yi et al. recently demonstrated that exfoliation of graphite by mild sonication in an aqueous solution of acetone with tailored Hansen solubility parameters gave highly concentrated (up to 0.21 mg/mL) and stable graphene dispersion [24]. A recent work by other researchers showed that aqueous graphene dispersions with high concentrations (up to 1 mg/mL) could be prepared by simultaneous exfoliation and stabilization under mild ultrasonic treatment in the presence of non-ionic surfactants [25]. Among the different molecules investigated, polyethylene glycol sorbitan monooleate (i.e. Tween-80) was one of the best candidates for effective dispersion of graphitic material [25].

A challenge concerning inkjet printing of graphitic material such as graphene is to find a solvent that not only satisfies the physical requirements (e.g. viscosity, density and surface tension) set by the printer but also allows to prepare stable dispersions. In addition, potential hazards to human health and the environment should also be taken into account. In most work, only mono- [19,20,22] or biphasic solvent systems [9,21] have been investigated, with limited possibilities to tailor the physical characteristics of the ink. Unfortunately, this is particularly important when thermal inkjet printing is applied due to limited possibilities to adjust the jetting quality by changing instrumental parameters. In this work, these issues were addressed by using an environmental-friendly aqueous ternary solvent systems (2-propanol and ethyleneglycol) for the preparation of stable dispersions of colloidal graphitic material. A comprehensive mapping of the physical properties (i.e. viscosity, density, surface tension) of different mixture compositions was performed. Hence, the mixture that best fitted the requirements of the thermal DOD inkjet printer used here could be identified. In addition, theoretical considerations regarding stability of graphene particles in these solvent mixtures were evaluated based on the popular Hansen solubility concept [26]. The final printable ink was prepared by dispersing colloidal graphitic material in the chosen solvent mixture. The colloidal particles were obtained by size reduction/exfoliation of graphite by means of wet grinding in the presence of a non-ionic surfactant (Tween-80, [25]). The yield of submicron particles obtained by grinding was evaluated using laser diffraction whereas the degree of exfoliation was approximated using X-ray powder diffraction (XRPD) and line broadening analyses. The results presented here allow to tailor physical properties of inks which offers great versatility towards different printing systems.

2. Experimental

2.1. Materials and experimental procedures

A commercial graphite powder (Sigma-Aldrich, <20 μm) was used as starting material for the preparation of the ink. Size reduction of this powder was accomplished by wet milling according to the following procedure: A graphite suspension having a solid content of 5 wt.% was prepared using an aqueous solution of