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Citation for published version (APA):

Arapov, K., Goryachev, A., With, de, G., & Friedrich, H. (2015). A simple and flexible route to large-area conductive transparent graphene thin-films. *Synthetic Metals*, 201, 67-75.
<https://doi.org/10.1016/j.synthmet.2015.01.016>

DOI:

[10.1016/j.synthmet.2015.01.016](https://doi.org/10.1016/j.synthmet.2015.01.016)

Document status and date:

Published: 01/01/2015

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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A simple and flexible route to large-area conductive transparent graphene thin-films

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ARTICLE INFO

Article history:

Received 1 August 2014

Received in revised form 22 December 2014

Accepted 8 January 2015

Available online xxx

Keywords:

Self-assembly

Large area graphene films

Lift-up transfer

p-Doping

XPS

ABSTRACT

Solution-processed conductive, flexible and transparent graphene thin films continue drawing attention from science and technology due to their potential for many electrical applications. Here, an up-scalable method for the solution processing of graphite to graphene and further to self-assembled large-area conductive transparent thin-films is presented. The method proceeds via the graphite intercalation route followed by thermal expansion to obtain expanded graphite. The resulting material is dispersed in a surfactant-free mixture of isopropanol and propylene glycol to obtain a stable colloidal dispersion. A graphene thin film is subsequently formed by self-organization at an oil/water interface followed by lift-up transfer to virtually any substrate of interest. Thermally annealed thin-films exhibit a thickness-tunable sheet resistances of between 10 and $0.8 \text{ k}\Omega/\square$ with transparencies between 75% and 45% at 500 nm wavelength, respectively. Additional Au-doping decreases the sheet resistance by a factor of 5. Heating doped films to temperatures above 380 K or exposure to ambient conditions significantly increases the sheet resistance as a result of decreasing charge carrier concentration. The presented method is a simple, up-scalable and thus competitive alternative to other techniques for large area graphene film production.

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1. Introduction

Conductive, flexible and transparent graphene thin films continue drawing attention from science and technology for electronic and photonic applications, e.g., to replace indium tin oxide (ITO) as transparent electrode. Fabrication techniques include chemical vapor deposition (CVD) [1,2], epitaxial decomposition of silicon carbide [3], and solution-processing [4–6]. The first two techniques require equipment such as vacuum chambers and high temperature furnaces and their associated low throughput, which so far has prevented wide industrial adoption. In contrast, solution-processing has penetrated further into the commercial sector as it is technologically simpler, inexpensive, and up-scalable. Here, the source for graphene dispersions is graphite, an abundantly available raw material. There are several solvent-based routes to obtain graphene dispersion from graphite, e.g., by extended ultrasonication [7], high shear mixing [6], by intercalation [8–13], or chemical modification [14–16]. The latter

includes oxidation of graphite to graphite oxide by Hummers' method and is followed by many research groups around the globe [17,18]. However, the oxidation leads to the formation of soluble but non-conductive graphene oxide intermediates, the conductivity of which can only be partially recovered by reduction. This restricts the use of (reduced) graphene oxide to those applications that only require moderate to low conductivities. The sonication route is generally inefficient [19] and often requires toxic solvents such as *N*-methylpyrrolidone [20] and *N,N*-dimethylformamide [21,22] or surfactants for stabilization of the graphene dispersion [23,24]. Extended ultrasonication of graphite in a mixture of two non-miscible solvent with significantly different surface tensions, e.g., water ($\gamma = 71.97 \text{ mN/m}$ at 25°C) and *n*-hexane ($\gamma = 18.40 \text{ mN/m}$ at 25°C) leads to partial exfoliation and entrapment of graphene on the liquid/liquid interface [25–27]. Graphene films produced by such a treatment are reported to be deprived of functional defects, however, control over the film thickness, reproducibility and film transfer is rather limited. The intercalation [8–13] route has shown potential for up-scalable production of large area graphene flakes, but it is again limited by the need for stabilization, mostly in toxic or surfactant containing solutions. Thus, there is a need for a high-

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throughput, environmentally benign and cost-effective route towards conductive transparent graphene thin-films, based on “wet chemistry”.

Here, we present a simple, efficient and up-scalable method starting from raw graphite for manufacturing large area graphene films by exfoliation, self-assembly and transfer by “lift-up”. The flexibility of the approach is illustrated by using both donor- and acceptor-type intercalation compounds as intermediates. Furthermore, we introduce a technique allowing deposition of a self-assembled film on glass, polymer or any other substrates of different shapes and area of more than 50 cm² and potentially more than 1 m².

2. Materials and methods

2.1. Synthesis of residue graphite bisulfate

Graphite was intercalated following Rüdorff's technique using sulfuric acid and potassium permanganate as oxidant [28]. This procedure predates Hummers method by 20 years and due to the stoichiometry of the reaction solution, an intercalation compound is formed instead of dispersible graphene oxide. The intercalation process can be written as:

The consequent sulfuric acid replacement can be written as:

In a typical synthesis 2 g of –10 mesh graphite (0.167 mol, Alfa Aesar, USA or Asbury Graphite, USA) were transferred to a flask containing 20 ml of concentrated sulfuric acid (Sigma–Aldrich, USA) and a PTFE coated magnetic stirrer. Under vigorous stirring, which creates a homogeneous slurry, 0.22 g of KMnO₄ were added to the flask at once and the mixture was left stirring for another 4 h. The resulting graphite bisulfate was hydrolyzed by transfer into 500 ml of distilled water. After an additional 4 h of stirring, the dispersion was left to settle and the precipitate was separated by decantation. Further three cycles of washing and consequent decantation were performed in order to remove the excess of sulfuric acid. Finally, the solid product was filtered off and washed with distilled water until a pH of 6 was reached. The final product was dried at room temperature for 24 h. The weight gain as defined by $\Delta m = ((m_{\text{RGB}} - m_{\text{C}})/m_{\text{C}}) \times 100\%$, where m_{RGB} is the mass of result residue graphite bisulfate, and m_{C} is the mass of starting graphite, was 51%, as expected. Crystallinity was analyzed by Bragg–Brentano X-ray powder diffractometer Rigaku Geigerflex using Lindemann capillaries with an internal diameter of 3 mm.

2.2. Synthesis of the Li–THF–GIC

The synthesis was performed using the procedure of Nomine and Bonnetain [29]. Tetrahydrofuran (THF) has been dried by refluxing with benzophenone and metallic sodium flakes, and then subjected to distillation. Then 1.28 g of naphthalene C₈H₁₀ (0.01 mol, Alfa Aesar, USA) were dissolved in 100 ml of freshly distilled THF by vigorous stirring followed by addition of 0.12 g of metallic lithium (0.017 mol, Alfa Aesar, USA) which was freshly cut and rinsed in hexane. Dissolution of lithium started with a delay of approximately 2 min required for charge transfer initiation. Subsequently the reaction mixture turned green followed by brown color with a green hue. Then 0.5 g of –10 mesh graphite (0.042 mol, Alfa Aesar, USA or Asbury Graphite, USA) were added to reaction mixture in one go. The reaction flask was then sealed and left stirring for 72 h. The Li–THF–GIC was separated from the side

products, i.e., colloidal naphthalene derivatives by decantation followed by rinsing with freshly distilled THF. The residue was filtered and dried in ambient conditions for 20 min. A weight gain of 30% was observed and crystallinity was analyzed as described above.

2.3. Thermal expansion of GICs

Typically, the microwave assisted thermal expansion was conducted for 1 min at 2450 MHz in a 700 W home appliance microwave oven. The GIC sample was placed at the bottom of Vitreosil quartz crucible equipped with a cup in a layer of ca. 3–5 mm, ensuring that all particles are in mutual contact. Along with the crucible it is necessary to place a beaker with ca. 100–200 ml of cold water as an energy drain to prolong the lifetime of the magnetron. Irradiation instantly causes fuming, red incandescence accompanied by sparks, and a remarkable volume expansion. After cooling the fluffy product was transferred to a glass container and used further without further treatment. The material was analyzed by means of XRD as described above and scanning electron microscopy (Philips XL30 FEG or FEI Quanta 3D FEG, operated at 5 kV).

2.4. Liquid phase exfoliation of expanded graphite

In a typical preparation, 1 mg of expanded graphite was added to 50 ml round bottom flask containing 10 ml of mixture of 3:2 (vol./vol.) isopropanol and propylene glycol. The dispersion was sonicated (Branson 1510 sonication bath, 70 W) for 1 h in ice water to obtain a deep dark colloidal stable dispersion. The quality of exfoliation was investigated by means of TEM (FEI Tecnai G2, 200 kV) and cryoTEM (FEI Titan Krios, 300 kV).

For additional details on Materials and methods, see the Supporting information: film self-assembly and transfer (page 2), electrical characterization (page 3), optical characterization (page 3), and XPS measurements (Page 3–4).

3. Results and discussion

3.1. Graphite exfoliation via intercalation

Exfoliation starts (Fig. 1a) from raw graphite. To alleviate exfoliation one has to weaken the interaction between the graphene layers by increasing their inter-planar distance. In this work both donor and acceptor-type graphite intercalation compounds (GIC) are utilized. Donor-type GICs are formed by the insertion of cationic species between graphene layers, whereas the graphite matrix becomes negatively charged resembling a macro-anion. Similar to that, for an acceptor-type GIC the graphite matrix is positively charged, stabilized by negatively charged intercalants. While most publications use either a donor-type or an acceptor-type GIC as a starting material to graphene, very few papers offer a direct comparison of thin films prepared from both types of material particularly following the same general route. The performance of the thin films are evaluated by conductivity and transparency measurements of donor-type LiC_{6–18}(THF)_{3,4–1,4} [30] (Li–THF–GIC) and acceptor-type residue graphite bisulfate (RGB–GIC) [31–35]. The preparation of the two GICs has been carried out following Rüdorff's procedure for graphite bisulfate GIC C⁺₂₄HSO₄[–] × 2–2.5H₂SO₄ [28] and the Nomine and Bonnetain [29] procedure for Li–THF–GIC. To minimize the amount of sulfur throughout the process we opt for hydrolyzed graphite bisulfate, an intercalation compound where most of the sulfuric acid is replaced by water [28,31]. We consider this step as beneficial due to the significantly decreased acidity of the synthesized material

Fig. 1. Graphite modification scheme. (a) A general scheme of graphene dispersion preparation starting from raw graphite; scanning electron micrograph of (b, c) Li-THF-GIC, and expanded graphite, (e, f) Residue graphite bisulfate, and expanded graphite. Transmission electron micrograph of (d) few layer graphene obtained from donor-type GIC, (g) few layer graphene obtained from acceptor-type GIC, (h) surfactant-free graphene dispersion with concentration of 0.1 mg/ml prepared from acceptor-type GIC.

along with an improved stability to decomposition in conditions of ambient humidity.

The structure of Li-THF-GIC is not stable and in time degrades to a mixture of graphite and Li-derivatives after already 1 h of exposure to an ambient conditions [36]. Therefore, the synthesized materials have been analyzed immediately after preparation and their structure was confirmed by XRD (Fig. S2) to be mainly a stage 1 compound with traces of higher stages [28,32,37]. Scanning electron microscopy (SEM) revealed that the morphology of the Li-THF-GIC only slightly different from the initial graphite (Fig. 1b), whereas RGB appears significantly swollen (Fig. 1e).

To increase the carbon interplanar spacing even more, the GICs were subjected to thermal expansion using a home appliance microwave oven. High-speed heating of the GIC results in abrupt conversion of intercalated species to the gas phase. The rapidly expanding gases cause a significant increase of the distance between the graphene layers equivalent to expansion along the [0001] crystallographic direction. In the literature this process is commonly referred to as “thermal shock” [38,39]. The rate of thermal shock defines the degree of expansion, which in turn, defines the degree of exfoliation (single sheets or few sheets stacked together; sheet area, etc.). The use of a microwave oven speeds up the thermal shock by the direct interaction of microwaves with the polar intercalants (e.g. H_2O , SO_4^{2-} , Li-THF) due to their high relative permittivity while hardly having any interaction with the low relative permittivity graphite matrix. Irradiation of the GICs instantly causes fuming, red incandescence accompanied by sparks, and a remarkable volume expansion.

A characteristic porous worm-like structure with almost detached layers has been observed by SEM for both materials, as summarized in Fig. 1 and S3. Acceptor-type expanded graphite (EG) has a highly porous sponge-like structure with clearly

distinguishable stacks of layers (Fig. 1f) while donor-type EG exhibits a structure with layers collapsed into balloons (Fig. 1c). X-ray diffraction for both donor and acceptor-type derived EGs showed a halo in the 2θ region between 10° and 40° , indicating a fully disordered structure of the previously Bernal-stacked layers (Fig. S2). It has been observed by, e.g., Strano and co-workers [9] as well as by us that expanded graphites prepared from different GICs do not restack into the original graphitic ordering after removal of the intercalants. This can be attributed to sheet corrugations. For graphene sheets on a substrate, corrugation has been found to be dependent on the stress state of graphene sheet and stress can be compensated by increasing sheet corrugation rather than by reduction of the C–C bond length [40]. For free standing graphene sheets, corrugation results from free energy minimization [41,42]. Moreover, any inhomogeneity will lead to differential thermal stresses, also capable of deforming the graphene sheets.

In the next step, the EG is exfoliated in the liquid phase [7]. Unlike graphene oxide – a non-conductive product of harsh graphite oxidation – pristine graphene is not soluble in either polar or non-polar solvents. However, it is dispersible in some solvents and mixtures up to a certain concentration [43]. We consider efficient dispersion as a key to material exfoliation whereas the instability upon interaction with an antisolvent can be utilized as a driving force for the film-assembly. We found experimentally that an optimal medium for exfoliation is a mixture of 3:2 (vol. ratio) isopropanol and propylene glycol (Fig. 1h) facilitating dispersions of up to 0.1 mg/ml of graphene which are stable for several weeks. The exfoliation products were investigated by transmission electron microscopy (TEM). Fig. 1d and g and S3 and S4 show well-exfoliated few-layer graphene membranes of several micrometers in largest dimension. It is interesting to note, that dispersions prepared from both donor and acceptor-type derived

expanded graphites showed no difference in quality and colloidal stability.

All dispersions are colloidally stable for at least one week if stored at room temperature and up to 1 month at 4 °C or below. More importantly, the resulting graphene dispersions are less toxic [44] and water-miscible which allows the formulation of graphene-based conductive paints, inks or, as reported here, assembly of large area thin-films. The obtained dispersions were used for film preparation without further purification steps. Cryo-TEM images of a resulting dispersion are shown in Fig. S5.

3.2. Thin-film assembly and lift-up

Self-assembly of the graphene thin films has been performed by stepwise addition of a graphene dispersion to an oil/water interface [45]. This procedure can be considered as somewhat similar to film compression in LB type methods [4,5,45]. In order to control film assembly, an initial calibration is required. In Fig. 2a a plot of the isothermal surface pressure calculated as a function of the amount of added graphene dispersion to the interface is presented [46]. Operating in the region with increasing surface pressure we may reproducibly and accurately vary thickness and, thus, conductivity and transparency of the final thin films by adjusting the amount of the dispersion added to the oil/water interface. After the film has been assembled, it is transferred by lift-up to a hydrophilized substrate, as shown in Fig. 2b. In order to improve the water drain between the film and the substrate, the latter was tilted by about 3–5°. This configuration improves the deposition process and also reduces the drying time. Films were dried at 110 °C in ambient conditions. Examples of deposited films on polymeric and glass substrates are presented in Fig. 2c and d.

3.3. Thin-film characterization and performance

The surface morphology of large area films deposited on a glass substrate and annealed at 400 °C has been studied by SEM (Fig. 3a

and d). According to our observations, thin films are composed of overlapping graphene sheets with a small number of edges protruding out of the plane of films as shown in Fig. S2c and Sd, which is considered as a major contribution to the overall roughness [4,5,47]. Furthermore, Raman spectra (excitation wavelength 633 nm, Fig. 3c and f) for both types of films display an average ratio between the G and D bands ($I(G)$ and $I(D)$) intensities of about 7–8 indicating a significantly smaller number of defects than for graphene oxide [48–50]. The defects found by Raman are a result of the limited graphene sheet size since the film is composed of overlapping graphene flakes. The probability of having edges of sheets within the measurement area is very high as the spot size of the focused laser is approximately 2 μm and the flake size varies from 1 to 5 μm , which does not change during processing and is independent of whether the film has been prepared via a donor- or acceptor-type GIC. The positions of the G band (1580 cm^{-1}) and the 2D band ($2670 \pm 18\text{ cm}^{-1}$) confirm few-layer (3–8) graphene [51]. The full width of half maximum of 2D band (FWHM(2D)) for donor-type films equals to $83 \pm 8\text{ cm}^{-1}$ whereas for acceptor-type derived films it equals to $74 \pm 12\text{ cm}^{-1}$. The shapes of 2D peak for both types of films correspond to multiplets.

X-ray photoelectron spectroscopy (XPS) measurements for annealed films of donor- and acceptor-type films showed no traces of sulfur and lithium and only minute traces of oxygen containing functional groups (Fig. 3b and e for C1s spectra and Fig. S6a and Sb for survey and Li1s and S2p spectra). We also performed XPS measurements for as-prepared expanded graphite (Fig. S7). The C1s peak has an asymmetrical shape and can be perfectly fitted by a standard HOPG spectrum. The asymmetric shape, as well as the presence of $\pi-\pi^*$ shake-up signal, is attributed to the sp^2 hybridization state of carbon, whereas, in the case of reduced graphene oxide there will be a significant portion of sp^3 hybridized carbon and no $\pi-\pi^*$ shake-up signal [52,53]. This is a clear illustration that the presented route, even in the case of acceptor-type GIC, which some may consider to be resembling Hummers

Fig. 2. Graphene thin film self-assembly and lift-up. (a) Calculated isotherm of surface pressure as a function of graphene dispersion added on the oil/water interface [46], (b) a scheme of the film transfer setup by lift-up technique. Photographs of graphene film on (c) hydrophilic poly(ethylene terephthalate) (PET) substrate, (d) quartz substrate.

Fig. 3. Properties of self-assembled graphene thin films. Scanning electron micrographs, C1s X-ray photoelectron spectra (XPS), and Raman spectra (633 nm) of graphene films on glass substrates after annealing at 400 °C prepared from (a–c) acceptor-type GIC, (d–f) donor-type GIC.

method, actually avoids irreversible graphite/graphene oxidation, i.e., it creates an intercalation compound instead of graphene oxide [28].

It was observed that after drying, as-prepared films have large variations in sheet resistance between experiments but these variations in sheet resistance are eliminated by thermal annealing [47] at 400 °C in a flow of dry nitrogen. Thermal annealing is accompanied by an approximately 60 fold increase in conductivity for both acceptor and donor-type derived films. This leads to large area thin films with resistances down to 800 $\Omega/\square$. Our observation that thermal annealing in the absence of oxygen functionalities (observed for donor and acceptor type films equally) results in a 60 fold increase in conductivity strongly suggests that the increase in film conductivity is not at all related to recovering the conductive properties of a non-conductive intermediate. Instead, it points towards a structural rearrangement in the tiled thin-films occurring during thermal annealing. This hypothesis is supported by *ex-situ* electron microscopy and diffraction studies before and after annealing the thin film. Self-assembled graphene films were deposited on TEM finder grids by lift-up and images and diffraction patterns of exactly the same areas (same acquisition conditions) before and after annealing were compared. As can be seen in Fig. S8a and Sb, changes in the moiré pattern are apparent after annealing already indicating rearrangements in the tiled film. The corresponding selected area electron diffraction patterns (Fig. S8c and Sd) clearly show differences in the relative intensity and position and while some diffraction spots appear and disappear upon annealing. This is strong evidence that by annealing not the individual graphene sheets change, but their relative position and orientation, which we refer to as structural rearrangement.

To study the relationship of conductivity and transparency in more detail a number of thin films of varying thickness (and thus conductivity and transparency) were prepared from donor and

acceptor type suspensions. For all films the sheet resistance (R_s) and light transmittance at 500 nm wavelength (T_{500}) was analyzed (Fig. 4a and b). These results indicate that the properties of our pristine films are comparable to the best results reported for films obtained by LB film deposition [5,47] (Fig. S8 for the wavelength dependence of transmittance). A quantitative comparison of the two sets of R_s vs T_{500} curves using the *t*-test [54] shows that, the performance of donor and acceptor type thin films is identical, i.e., within the sampling error at the 5% significance level. Together with the XPS results one can conclude that after thermal annealing both routes lead to similar materials, i.e., expanded graphites without a significant amount of adsorbates. To investigate the electronic transport properties of our films further, we performed Hall-effect measurements (Fig. 5a).

The dependence of sheet resistance as a function of temperature is presented in Fig. 5b, and c (red curves) and Fig. S10. It can be clearly seen that with an increase in temperature the resistivity is decreasing indicating the semiconducting nature of the graphene film. For as-prepared films we observed two characteristic ranges of resistance: (i) from 300 K to ~380 K with a decrease of ~6 Ω/K and (ii) from 380 K to 570 K with a decrease of 10 Ω/K . The different behavior between the two ranges can be explained considering the carrier concentration. The carrier concentration plotted in Fig. 5b (black curve) reveals the presence of holes as majority carriers in the 300–380 K interval (p-doping) while from 380 K to 570 K electrons are the majority carriers. This switch of conductance from holes to electrons at the charge neutrality point (CNP, 380 K) can be attributed to water desorption at its boiling point. Annealing the sample *in-situ* in a flow of dry nitrogen and repeating the measurement (Fig. 5c) results in electrons being the majority carrier over the entire temperature range with a constant concentration of $2\text{--}3 \times 10^{13} \text{ cm}^{-2}$ [55]. Exposure of films to ambient conditions leads again to p-doping by airborne water

Fig. 4. Electronic transport properties of self-assembled graphene films. Sheet resistance vs transmittance at 500 nm for self-assembled graphene film prepared from (a) donor-type GIC, (b) acceptor-type GIC.

and a return to the pattern shown in Fig. 5b. Sheet resistances for films in ambient conditions and after annealing are presented in Fig. S11. Finally, donor and acceptor-type graphene films of the same transparency and conductivity exhibit almost identical electronic transport properties.

3.4. Au-doping and stability

There are several approaches to tune graphene electronic transport properties and the work function, including covalent modification of graphene framework [56], deposition of metals to generate Schottky-barrier type carrier injection [55,57], and non-covalent charge-transfer complex formation [58–62]. Due to simplicity and controllability, we choose the latter route and investigated the influence of AuCl_3 doping on self-assembled graphene thin film conductive properties. Au doping was carried out with a 15 mM solution of AuCl_3 in nitromethane that was spin-coated onto annealed films [58]. Immediately after Au-doping the films were transferred to the Hall effect setup and their electronic transport properties analyzed. The typical effect of doping was a decrease in sheet resistance of approximately 5 times at room temperature, i.e., a decrease from 5.5 kΩ/□ to slightly below 1 kΩ/□ (Fig. S10). Concomitant with doping, Raman spectroscopy (Fig. 6a) revealed a significant upshift of the G-band position (Pos

Fig. 5. Electronic transport properties of self-assembled initial graphene films. (a) Image of Ag-patterned self-assembled $2 \times 2 \text{ cm}^2$ graphene film sample in Hall-effect measurement holder. (b) sheet resistance (red) and carrier concentration (black) as a function of temperature for films measured after exposure to ambient conditions (room temperature, relative humidity above 50%), (c) sheet resistance (red) and carrier concentration (black) for the second heating run from room temperature without exposure to ambient conditions. (For interpretation of the

(G)) from 1580 cm^{-1} to $1612 \pm 4 \text{ cm}^{-1}$ along with a decrease in the 2D peak intensity [49,51].

From an application point of view the stability of the Au doping with temperature and in time when exposed to ambient conditions

are of the utmost importance. Heating of Au-doped thin films shows that the sheet resistance is increasing with increasing temperature which can be attributed to a metallic type of conduction (Fig. S10). Hall effect measurements revealed that upon doping holes are the majority carriers with concentrations of up to $1.3\text{--}1.6 \times 10^{14} \text{ cm}^{-2}$ (Fig. 7a and b, red curves). The majority carriers were thermally stable up to $\sim 400 \text{ K}$ (in a flow of dry N_2) followed by a sharp decrease down to the level of $3 \times 10^{13} \text{ cm}^{-2}$ at $\sim 475 \text{ K}$. We tentatively attribute this decrease to the conversion of AuCl_3 to AuCl at a temperature of 433 K (Fig. 6d). A second heating cycle in a flow of dry N_2 (Fig. 7a, blue curve) showed that the carrier concentration of films, previously heated to 550 K , was approximately constant at a level of $3 \times 10^{13} \text{ cm}^{-2}$. The sharp decrease in carrier concentration at temperatures between 400 K and 475 K was observed for both donor- and acceptor-type Au-doped thin-films. These results indicate (Fig. 7a, red curve) that in the temperature window below 380 K (conservative estimate) dopant concentration, i.e., number of Au^{3+} /graphene charge transfer complexes, is approximately constant. Heating the sample to higher temperatures decreases the number of Au-injected holes significantly. This process is followed by metal migration and formation of Au-nanoparticles as illustrated in Fig. S14 and as observed by others [58]. To prove thermal stability of doping until 380 K , a second set of measurements was performed. Heating of Au-doped films from 300 K to 380 K kept the hole concentration constant at about $1.5 \times 10^{14} \text{ cm}^{-2}$ and in the second heating cycle the same hole concentration was measured (Fig. 7b).

To support our conclusions we performed XPS analysis and determined the work function of Au-doped and annealed thin films (see SI). Spectra of C1s of doped and annealed at 380 K graphene

films revealed the presence of a shoulder (Fig. S12), which is tentatively attributed to a charge transfer complex between graphene and Au^{3+} . Furthermore, the Au 4f spectrum, as shown in Fig. 6b, has several components including Au^0 , Au^{3+} (major), Au^+ (minor) and Au_x (required for fitting), indicating a complex interaction between graphene and dopant. The presence of Au^0 is probably due to partial decomposition of AuCl_3 . An increase in the work function (absolute values given in Table 1, Fig. S13) of more than 1 eV , indicating the lowering of the Fermi level, is observed and confirming the charge transfer from graphene to Au^{3+} . Since the Au 4f spectra of a film annealed at 430 K show an increase in Au^+ species (Fig. 6c, Table 1), AuCl_3 decomposition to AuCl during annealing can be inferred. Furthermore, heating the Au-doped films to 575 K or higher leads to a decrease of the Au^+ and an increase of metallic Au relative concentrations (Fig. 6d).

The value of work function for graphene thin films (Table 1) found by XPS analysis is different from the values reported earlier [55,63]. We attribute this discrepancy to the influence of surface contaminations present on graphene films, as we did not perform any treatment (Ar^+ ablation, thermal annealing in UHV and so forth) prior to measurements.

To evaluate the effects of ambient conditions on the carrier concentration in-time, two sets of films, which had initially the same level of Au-doping were measured, i.e. the same initial carrier concentration (Fig. 7c). Over a 10 day period, a reference film was kept and measured in dry N_2 and a second film was analyzed in ambient conditions at a relative humidity of 50%. In agreement with previously reported trends [60], exposure of the Au-doped graphene thin-films to ambient conditions in our case halved the carrier concentration, i.e., increased the sheet resistance by a factor

Fig. 6. AuCl_3 -doped graphene films. (a) Raman spectra (excitation wavelength 633 nm) of initial film (black) and AuCl_3 doped film (red), XPS Au 4f spectra of AuCl_3 -doped film annealed at 100°C (b), 160°C (c), and 200°C (d). The component, marked as Au_x , is required for fitting. Its relative concentration ($\text{Au}_x/\text{Au}(\text{all})$) is maintained on the level of 5–7 percent and does not change throughout annealing experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Electronic transport properties of self-assembled AuCl_3 doped graphene films. (a) Dependence of carrier concentration on thermal treatment from 300 to 550 K: red curve – first *in situ* measurements, blue curve – second *in situ* measurement of annealed film from, black curve – initial film. Positive curve values refer to conduction by holes, negative ones to conduction by electrons. (b) Dependence of carrier concentration on thermal treatment from 300 to 380 K: red curve – first *in situ* measurements, blue curve – second *in situ* measurement of annealed film from, black curve – initial film. (c) Dependence of carrier concentration on exposure to different media: black squares – dry N_2 , red circles – ambient environment (relative humidity $\sim 50\%$). Error bars correspond to sample standard deviation of observed values within the set of analyzed films, typically using 5 data points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of 2. In this process also the temperature dependence of conductivity shifts from metallic for doped, non-heated films to semiconducting after ambient exposure as seen in Fig. S10. Here it is interesting to note that heating of films to 390 K after ambient conditions does not recover the initial carrier concentration. We hypothesize that the observed decrease in carrier concentration

Table 1

Relative concentrations of Au species and work function of doped films during thermal treatment.

Sample	Relative concentration (%)			Work function (eV ± 0.2 eV)
	Au^0/Au (all)	Au^{3+}/Au (all)	Au^+/ Au (all)	
Graphene film	–	–	–	4.9
Annealed @380 K	26.3	60.8	7.3	6.3
Annealed @430 K	29.9	47.8	15.4	6.0
Annealed @575 K	45.2	46.9	3.5	6.3

upon exposure to humid air and concomitant increase in sheet resistance can be attributed to the irreversible decomposition of Au^{3+} charge transfer complexes.

4. Conclusions

We have demonstrated a simple, fast, environmentally-friendly dispersion-based approach to self-organize and transfer graphene films onto various substrates, such as glass or plastic, using either a donor- or an acceptor-type graphite intercalation compound. We found that a mixture of 3:2 (vol.) of isopropanol and propylene glycol is the optimum to uniformly disperse graphene at a concentration of 0.1 mg/ml and use for thin film self-assembly. The colloidally stable (>1 month), non-toxic and water-miscible dispersions can be utilized not only for thin film self-assembly but also for the formulation of conductive paints and inks [64]. Independent of utilizing donor- or acceptor-type intermediates, thermally annealed thin films performed equally well in terms of sheet resistance and transmittance. Hence, annealing in the absence of oxygen functionalities points towards a structural rearrangement in the tiled thin-films occurring, leading to the 60 fold increase in conductivity rather than recovering the conductive properties of graphene oxide. Annealed and non-doped films exhibit sheet resistances in the range of $10 \text{ k}\Omega/\square$ at $T_{500} \sim 75\%$, $0.8 \text{ k}\Omega/\square$ at $T_{500} \sim 45\%$. A systematic investigation of Au-doping on the films conductive properties showed that via doping the sheet resistance can be decreased by a factor of 5. Nevertheless, concomitant with XPS studies we found a temperature processing limit for Au-doped films at 380 K which in turn will dictate the conditions for further treatments such as additional functional layers, e.g., in OLED devices. Also exposure of doped films to ambient conditions, i.e., 50% relative humidity, causes a significant drop in dopant concentration accompanied by a two-fold increase in sheet resistance. In summary, our flexible, inexpensive, and up-scalable method to graphene thin films, with and without doping, is a strong competitor to other techniques for the deposition of transparent and conductive layers in optoelectronic devices, gas sensors or printable electronics.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Program (FP7-MC-ITN) under grant agreement No. 264710. The authors would like to thank the Directorate-General for Science, Research and Development of the European Commission for financial support of the research.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.synthmet.2015.01.016>.

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