Properties of graphene inks stabilized by different functional groups

2011 Nanotechnology 22 245702

(http://iopscience.iop.org/0957-4484/22/24/245702)

IOP Publishing Nanotechnology
Nanotechnology **22** (2011) 245702 (7pp) doi:10.1088/0957-4484/22/24/245702

Properties of graphene inks stabilized by different functional groups

Di Wei[1], Hongwei Li[1], Dongxue Han[2], Qixian Zhang[2], Li Niu[2], Huafeng Yang[2], Chris Bower[1], Piers Andrew[1] and Tapani Ryhänen[1]

[1] Nokia Research Centre, Broers Building, 21 JJ Thomson Avenue, Cambridge CB3 0FA, UK
[2] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun City 130022, Jilin Province, People's Republic of China

E-mail: di.wei@nokia.com and lniu@ciac.jl.cn

Received 8 February 2011, in final form 17 March 2011
Published 20 April 2011
Online at stacks.iop.org/Nano/22/245702

Abstract
Different graphene inks have been synthesized by chemical methods. These uniform dispersions were stabilized by various functional groups such as room temperature ionic liquid, polyaniline, polyelectrolyte (poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt) and poly(styrenesulfonate) (PSS). The dispersions can be easily cast into high-quality, free-standing films but with very different physiochemical properties such as surface tension and adhesion. SEM and AFM methods have been applied to have a detailed study of the properties of the inks. It is found that graphenes modified by p-type polyaniline show the highest surface tension. Diverse surface adhesive properties to the substrate are also found with various functional groups. The different viscoelasticities of graphene inks were related to the microscopic structure of their coating layer and subsequently related to the configuration, chemistry and molecular dimensions of the modifying molecules to establish the property–structure relationship. Modifications of graphene inks made from chemical reduction cannot only enable cost-effective processing for printable electronics but also extend the applications into, for example, self-assembly of graphene via bottom-up nano-architecture and surface energy engineering of the graphenes. To fabricate useful devices, understanding the surface properties of graphene inks is very important. It is the first paper of this kind to study the surface tension and adhesion of graphene influenced by different functional groups.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Unlike the 1D carbon nanotube, graphene is a material which consists of a 2D layer of sp^2-hybridized carbon atoms bonded together and the shape that results from it is a 'honeycomb' lattice, notable for its high regularity and unique physical properties. In the form of nanosheets with lateral sizes in the range of several hundred nanometres, graphene exhibits superior electrical conductivity, high charge carrier mobility ($20\ m^2\ V^{-1}\ s^{-1}$) [1, 2], fascinating transport phenomena such as the quantum Hall effect and high surface areas of over $2600\ m^2\ g^{-1}$ [1, 2]. It is attracting growing interest from the scientific community [3] due to the recent advances that have led to the award of the Nobel Prize in physics in 2010 [4]. While much interesting work has been carried out on the manufacturing of graphene samples by mechanical or liquid-phase exfoliation [5, 6], chemical vapour deposition [7, 8] and thermal decomposition of SiC [9], for many applications it is necessary to develop high-yield, cost-effective, reproducible and mass-production methods. Large scale exfoliation of graphene oxide (GO) has been reported [10]. GO is highly exfoliated and very stable when dispersed in aqueous solutions. Such dispersions are very useful as they facilitate both materials processing and fundamental characterization.

Chemically derived GO offers many applications in thin film electronics and optoelectronics covering sensors, transistors, memory devices, solar cells, etc [11]. However, GO itself is a poor electrical conductor, but fortunately the oxide can be removed by chemical reduction [12]. This adds another step in the processing procedure of pure graphene solutions. Large-area ultrathin films of such reduced GO can be made as a transparent and flexible electronic material [13]. Graphene inks formed by such chemical reduction methods from GO can also be modified simultaneously with different functional groups. Modifications can also improve the water solubility of graphene dispersions [14, 15].

Surface functionalization of graphene is necessary both for the modification of their properties and the acquisition of new characteristics. To make full use of the excellent electrical and mechanical properties of graphene and to realize the full potential of graphene-based nanocomposites and nanodevices, graphene inks with different functional groups were studied in this paper characterized with different physiochemical properties. This could provide some reference and guidance to make appropriate and promising applications of graphene inks based on their tunable and controllable physical properties. This study will further extend the scope for scalable liquid-phase manufacturing and processing (e.g. printing) of graphenes for a wider range of applications.

2. Experimental details

All the modified graphene inks reported are based on the chemical reduction of the exfoliated graphene oxide (GO) described below.

2.1. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared by oxidizing natural graphite powder (SP, 320 mesh) based on a modified Hummers method as originally presented by Kovtyukhova and colleagues. As-prepared graphene oxide was suspended in ultra-pure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids for four days. The resulting purified graphene oxide powder was collected by centrifugation and then air-dried. Graphene oxide powder was dispersed in water to create a 0.05 wt% dispersion. Then the dispersion was exfoliated through ultrasonication for 1 h, during which process the bulk GO powder was transformed into GO nanoplatelets.

2.2. KOH-treated graphene

Graphene oxide (GO) was synthesized from natural graphite powder (SP, 320 mesh) by a modified Hummers method. As-prepared GO was purified via dialysis for four days. In a typical procedure for chemical re-graphitization by KOH, 10 ml of the aqueous GO dispersion ($0.5\ \mathrm{mg\,ml^{-1}}$) was mixed with 10 mg KOH (82%, Tianjin Chemicals, China) in a 50 ml flask, and a homogeneous yellow suspension was obtained. After ultrasonication for a few minutes, the yellow suspension changed to a homogeneous yellow-black dispersion. Then, the flask was put in a oil bath (∼80 °C) for 24 h. During refluxing, the yellow-black suspension became black when adding the reducing agent of hydrazine solution in water (50%). A homogeneous long-term-stable black graphene nanosheet dispersion was obtained after 24 h.

2.3. Preparation of polydisperse chemically converted graphene nanosheets functionalized with room temperature ionic liquid (IL)

3-bromopropylamine hydrobromide (1.1 g, 5 mM) and 1-methylimidazole (0.395 ml, 5 mM) were added to 12.5 ml ethanol, forming a colourless solution which was refluxed under nitrogen for 24 h. The resulting turbid mixture was purified by recrystallization from ethanol, with ethyl acetate as the anti-solvent. Finally, the resulting white powder was dried under vacuum at 60 °C overnight and then purified. 1H NMR (D2O): = 8.738 ppm (S, 1H), 7.484 ppm (S, 1H), 7.424 ppm (S, 1H), 4.283 ppm (t, 2H), 3.022 ppm (t, 2H) and 2.232 ppm (m, 2H). IL-$\mathrm{NH_2}$ is soluble in DMF and DMSO, and well soluble in water, and stable in air. Polydisperse chemically converted graphene nanosheets were synthesized by an epoxide ring-opening reaction between graphene oxide (GO) and 1-(3-aminopropyl)-3-methylimidazolium bromide (IL-$\mathrm{NH_2}$). Firstly, IL–$\mathrm{NH_2}$ (10 mg) was added to 10 ml of the homogeneous and transparent GO dispersion in water ($0.5\ \mathrm{mg\,ml^{-1}}$), and then the salt effect of the GO sheets occurred, owing to the presence of the ionic liquid. Secondly, KOH (20–30 mg) was added to the above turbid mixture and then the mixture was subjected to ultrasonication for 30 min. After ultrasonication, the turbid mixture was transformed into a homogeneous and transparent solution. Finally, the homogeneous solution was vigorously stirred at 80 °C for 24 h. The resulting polydisperse chemically converted graphene was subsequently centrifuged, washed with ethanol and water, and air-dried.

2.4. Synthesis of polyelectrolyte and poly(sodium 4-styrenesulfonate)-modified graphene

First, 20 mg of as-prepared GO was distributed in 40 ml of ultra-pure water and mixed in an ultrasonic bath (KQ218, 60W) for 15 min to obtain a homogeneous and stable dispersion. Following this, 60 mg of an ionic polymeric binder (such as polystyrenesulfonate) or poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt was added to the graphene oxide dispersion and mixed in an ultrasonic bath (KQ218, 60W) for another 15 min. The resulting mixture was then reduced by hydrazine monohydrate (1.950 ml, 50%) at 80 °C for 24 h to obtain a homogeneous black-coloured dispersion. This dispersion was then filtered through a polycarbonate membrane (0.22 μm pore size) and repeatedly washed with water to remove any excess binder/free ionic fluid (polymer). The resulting powder (comprising graphene platelets modified by these polymers) was then redistributed in water by ultrasonication in a water bath (KQ218, 60W) for 15 min and centrifuged at 5000 rpm for

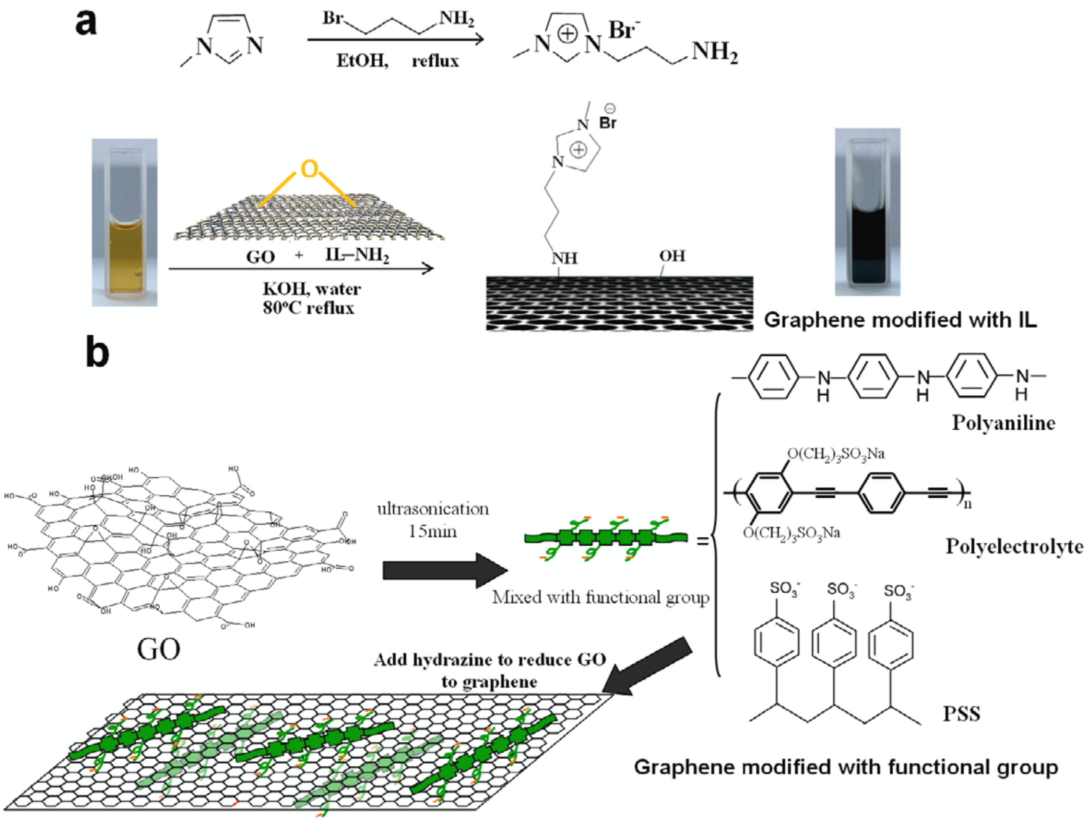

Figure 1. Different chemical structures of the graphene inks: (a) graphene functionalized by ionic liquid (IL) and (b) graphene modified by different functional groups of polyaniline, polyelectrolyte and PSS anions.

20 min. A dark, homogeneous supernatant solution was obtained after removing the sediment.

2.5. PANI-modified graphene

In a typical hierarchically structured polyaniline synthesis, 5 ml brown GO dispersion was added to 10 ml of 0.05 mol l^{-1} aniline and 0.1 mol l^{-1} H_2SO_4 aqueous solution, under ambient conditions with vigorous stirring. 1 ml of aqueous ammonium peroxydisulfate (APS) (0.2 mol l^{-1}) as the oxidant was added dropwise to the mixture over the course of one minute. The resulting green material was rinsed with distilled water and methanol several times and collected via centrifugation at 5000 rpm after 24 h stirring. The washed residue was dispersed in 30 ml of water. An adopted method to reduce GO to graphene was used here. 5 μl of hydrazine solution was added to 25 ml of the resulting dispersion. After being vigorously stirred for a few minutes, the flask was put in an oil bath (95 °C) for 1 h. A blue dispersion was obtained instead of the black graphene solution. The obtained, as-prepared hierarchically structured polyaniline (HSPAN) can be re-dispersed readily in cold water with the aid of ultrasonication.

All graphene ink samples were placed in a sonic bath for 15 min prior to contact angle measurement. Advancing and receding contact angles on a clean Si wafer were measured using a CAM 2000 contact angle goniometer, by pumping ~1.3 μl drops of each solution at a rate of 2 μl s^{-1} onto the Si wafer then pumping the drop back into the syringe, whilst capturing a total of 40 images at a rate of 1 s^{-1}. Measurement of the contact angles on both the left and right side of the drop were made by fitting a polynomial to the droplet edge using the CAM 2000 software. Raman spectra were obtained with a Raman system (Renishaw model 1000) using an argon ion laser (514.5 nm) as the excitation source.

3. Results and discussion

Due to its exceptional properties, various applications of graphene have been investigated, including batteries [16], supercapacitors [17], field effect transistors [18] and logic devices [19]. To fabricate useful devices, understanding the surface properties of graphene is very important. Contact deposition is critical to device performance and functionality. However, contact deposition often fails because of graphene's hydrophobic nature. Although it is a very important area to know how to tune the wettability of graphene inks, there are quite a few studies investigating the surface properties of this material. Only recently it was reported that the wettability of graphene is improved without additional damage by using low-power oxygen plasma treatment. This can somehow solve the adhesion issues involved in the fabrication of graphene devices [20]. To further fine tune the wettability, this paper studied the graphene inks with various functional groups.

Different structures of the synthesized graphene inks are shown in figure 1. Polydisperse chemically converted

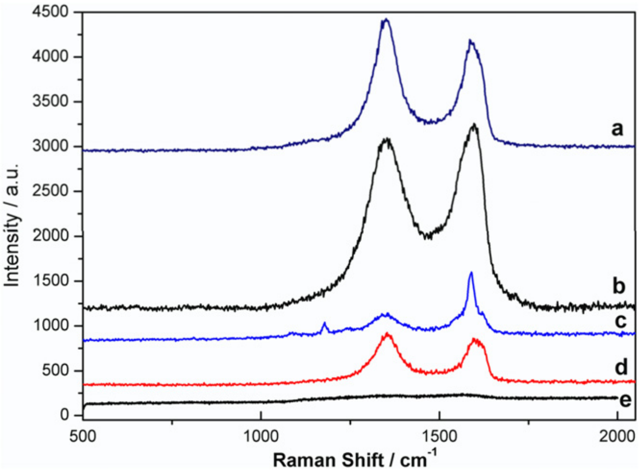

Figure 2. Raman spectra of (a) IL-modified graphene, (b) KOH-exfoliated graphene, (c) polyelectrolyte-modified graphene, (d) PSS-modified graphene and (e) polyaniline-modified graphene solution.

graphene nanosheets (figure 1(a)) were formed by an epoxide ring-opening reaction between GO and a room temperature ionic liquid (IL) (1-(3-aminopropyl)-3-methylimidazolium bromide) and results in a well dispersible graphene-based material that has long-term stability [21]. Only in this ink is amine-terminated IL covalently functionalized on the graphene sheet, while other functional groups reported here such as polyelectrolyte (poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt), PSS (polystyrenesulfonate) and polyaniline are attached to the reduced graphene flake by van der Waals forces. Intermolecular attractions of van der Waals forces attract these functional groups on the graphene sheets during chemical reduction by hydrazine. They formed black uniform dispersions as well like in figure 1(a).

Raman spectra were measured for each chemically modified graphene sample using an argon ion laser (514.5 nm) as the excitation source. The laser power at the sample position was typically 400 μW with an average spot size 1 μm in diameter. The D and G bands, which lie at around 1360 and 1580 cm^{-1}, respectively, are common features for carbon-based materials. The intensity ratio between the D and G bands (I_D/I_G) has been used as a measure of disorder in graphene. When I_D/I_G increases, covalent bonding or a strong interaction of functional groups with graphene layers happens. This is the case for IL-modified graphene (figure 2(a)), which is indeed a covalent bonding of the ionic liquid onto graphene sheets and PSS-modified graphene (figure 2(d)), where PSS may have a stronger interaction with graphene layers. Both processes induce defects. In contrast, the graphene exfoliated from KOH solution (figure 2(b)) has fewer defects. The dramatic decrease in I_D/I_G for polyelectrolyte-modified graphene (figure 2(c)) indicates that the polyelectrolyte-functional group greatly enhances the intensity of the G band of graphene sheets due to its conjugated structure. It is very hard to take the Raman spectra for polyaniline-modified graphenes and there is large noise interference to overlap the characteristic D and G bands as figure 2(e) shows.

When these types of graphene inks were deposited on an Si substrate, they showed very different surface tensions. As shown in figure 2, each type of as-prepared graphene ink is drop-cast on the Si chip (1 cm × 1 cm) at room temperature (25 °C).

Most properties of graphene are sensitive to the number of layers. However, the contact angle results showed that the property of wettability is independent of the thickness: in other words, the contact angle does not have much correlation with the number of layers of graphene in the solution [20]. Thus the different wettability of the ink shown in figure 3 may be mainly influenced by the different functional groups. After the samples were dried, SEM images were taken to study the surface morphology of the deposit as shown in figure 4.

Figure 4(b) is the SEM image from the only graphene ink modified by inorganic KOH solution, which shows a very rough surface. Such an ink also has a similar low surface contact angle (figure 3(Ib)) to the water-soluble PSS-anion-modified graphene ink (figure 3(Id)). Advancing and receding contact angles of the inks were measured on a clean Si wafer using a CAM 2000 contact angle goniometer. Measurement of the contact angles on both the left and right side of the drop were made by fitting a polynomial to the droplet edge using the CAM 2000 software. The data are listed in table 1. Figures 3(a), (c)–(e) are the SEM images for graphene inks modified with organic functional groups. The surface contact angles of the inks modified with larger, more hydrophobic organic groups (i.e. IL in figure 3(Ia), polyelectrolyte in

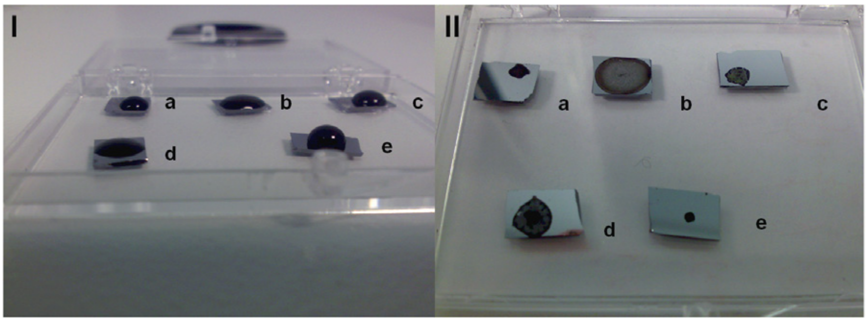

Figure 3. Drops of graphene inks on Si substrate with different surface tensions (I) after being drop-cast and (II) when dried. (a) IL-modified graphene, (b) KOH-exfoliated graphene, (c) polyelectrolyte-modified graphene, (d) PSS-modified graphene and (e) polyaniline-modified graphene.

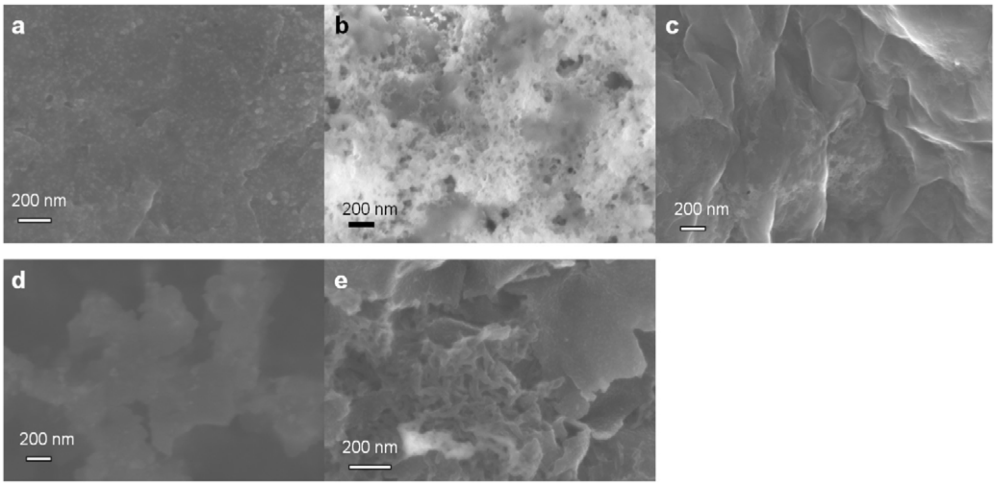

Figure 4. SEM images of (a) IL-modified graphene, (b) KOH-exfoliated graphene, (c) polyelectrolyte-modified graphene, (d) PSS-modified graphene and (e) polyaniline-modified graphene.

Table 1. Advancing and receding contact angles of the graphene inks. (a) IL-modified graphene, (b) KOH-exfoliated graphene, (c) polyelectrolyte-modified graphene, (d) PSS-modified graphene and (e) polyaniline-modified graphene.

	Ink a	Ink b	Ink c	Ink d	Ink e
Advancing contact angle (deg)	53	27	52	13	98
Receding contact angle (deg)	44	21	46	12	84

figure 3(Ic) and polyaniline in figure 3(Ie)) are larger than those of the inks modified with KOH (figure 3(Ib)) and the water-soluble PSS anion (figure 3(Id)). Adding a surfactant functional group such as PSS can decrease the contact angle to 13° with the least hysteresis between advancing and receding contact angles. Among the graphenes with organic functional groups, the one modified with polyaniline has the highest contact angle and shrinks to a tidy ball when dried (figure 3(IIe)). It also has the highest hysteresis as shown in table 1. The inks in the end are dried at 1 atm pressure and room temperature in air. The SEM image of its structure (figure 4(e)) shows the polyaniline nanofibres holding the graphene flakes tightly together. The peel-off test shows that the dried polyaniline graphene is easily peeled off from the substrate. It is generally accepted that good wettability results in good adhesion. From the results shown in figure 3 and table 1, KOH (b) and PSS (d) modified graphene inks have better adhesion compared to the other inks.

Atomic force microscopy (AFM) measurement has also been employed to characterize the surface morphology and molecular interaction of these inks when dried. The results are shown in figure 5. AFM imaging of graphene has been carried out in tapping mode and force curves are taken over the image area of the samples with a scan area of 2 μm × 2 μm. For all those samples, the surface morphologies by AFM confirm the results by SEM.

Due to the high concentrations of graphene in the suspensions, they are not dispersed as monolayers when drop-cast on an Si substrate. The interesting point to be noticed here is the differences in all the force curves which are determined by hardness of the material and the surface adhesive properties, and therefore mostly by the modification groups attached to it. Figure 4(a) shows the morphology of the pristine Si chip. The force curves demonstrate a typical intermolecular interaction between the AFM tip and the rigid Si substrate. The force curve of KOH-exfoliated graphene (figure 5(c)) is very similar to that on bare silicon (figure 5(a)), which means the graphene is quite solid and its surface is not sticky. The force curves from organic-group-modified graphenes are quite different from each other and from the KOH-modified one. Force curves from polyelectrolyte- (figure 5(d)) and PSS- (figure 5(e)) modified graphene are similar but have obvious higher adhesive forces to the AFM tip than KOH-modified ones. This is clearly shown by the large pull-off distance on the retraction curve. The large heterosis on the force curves of IL- (figure 5(b)) and polyaniline-(figure 5(f)) modified graphene indicated that both of them are very soft, but there is still a difference between them. The IL-modified sample shows no pull-off force while the polyaniline-modified one has clear adhesive force. Thus IL-and polyaniline-modified graphene inks show a more ‘organic’ soft nature and shrink to a small dot when dried (figures 3(IIa) and (IIe)) but the polyaniline-modified graphene has a stronger intermolecular adhesive force and aggregates to a tiny ball when dried. This, on the other hand, makes it easiest to be peeled off from the Si substrate.

Understanding the surface characteristics, adhesion and controlling the wettability of graphene are very important for many applications. The graphene surface is known to be hydrophobic, and oxygen plasma treatment with optimized power and duration has been proposed to control the adhesive properties for contact fabrication of graphene [20]. There exists a correlation between the level of defects and the contact angle. As more defects are induced, the surface energy of graphene is increased, leading to a more hydrophilic

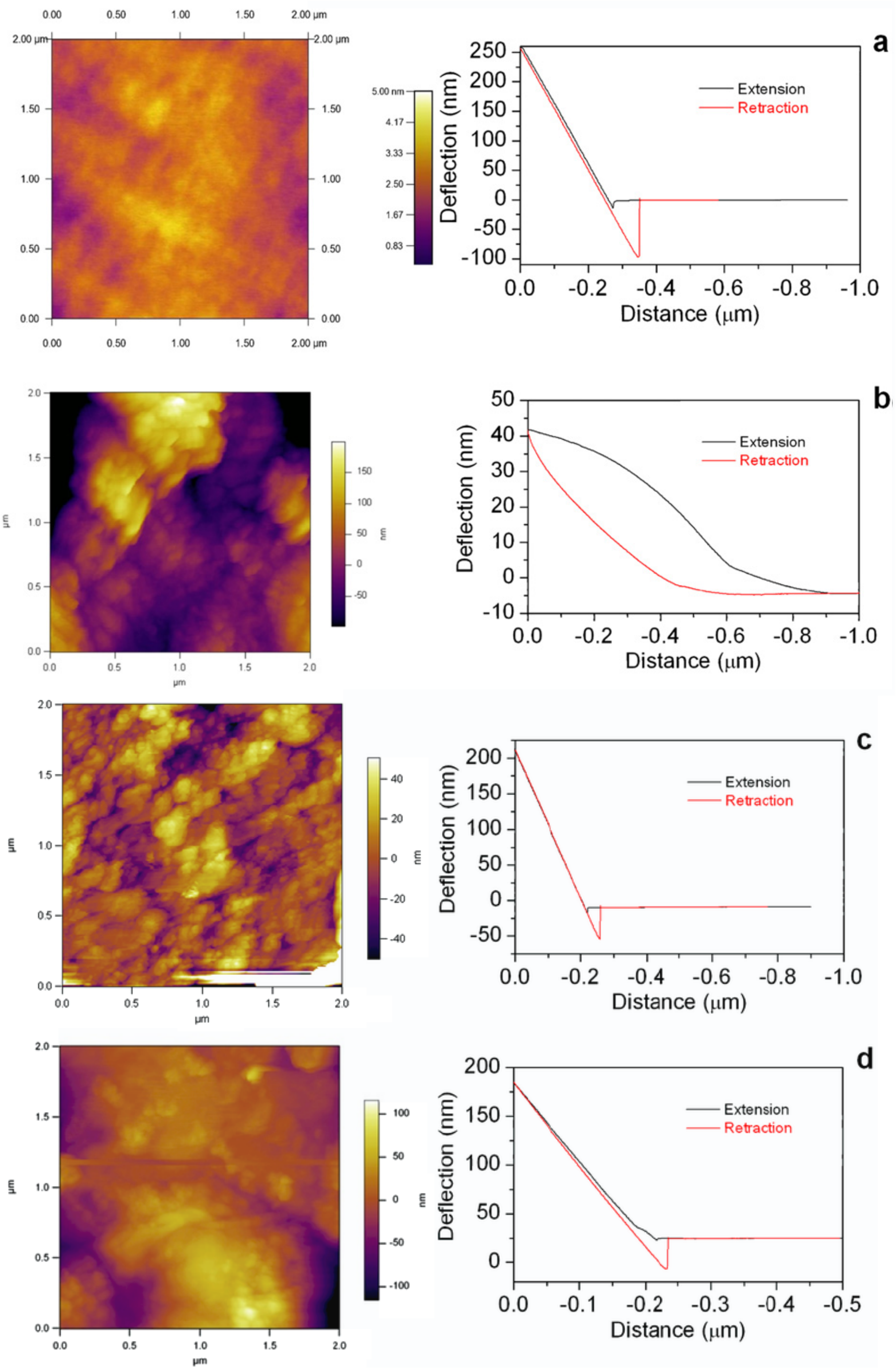

Figure 5. AFM and force curve of (a) pure Si substrate, (b) IL-modified graphene, (c) KOH-exfoliated graphene, (d) polyelectrolyte-modified graphene, (e) PSS-modified graphene and (f) polyaniline-modified graphene.

nature. In this paper, we proposed an alternative way of tuning the surface energy by different functional groups attached to the graphenes. Different organic functional groups with different polarities impart different wettabilities of the modified graphene inks. Surfactant (e.g. PSS anion)-modified graphene inks are stable and have the best wettability (lowest contact angle among five graphene inks) and thus very good adhesion to the substrate.

With further surface modifications, graphene inks can be tuned to any property suitable for their specific use, thereby further expediting the applications in composite materials, emissive displays, micromechanical resonators, field effect transistors and ultrasensitive chemical detectors. It also paves the way for surface energy engineering of graphene modified by different functional groups. In summary, this approach is scalable (allowing the possibility of high-volume production) and versatile (in terms of being well suited to chemical functionalization). These advantages mean that the colloidal suspension method for producing graphene could be used for a wide range of applications. In the form of a colloidal

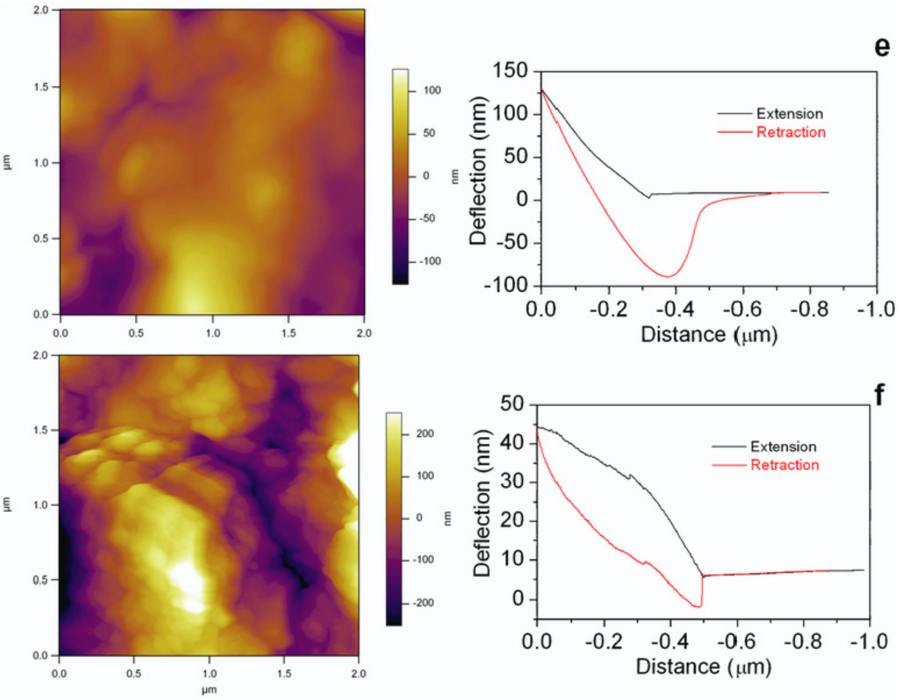

Figure 5. (Continued.)

suspension, graphene is also a non-toxic nanomaterial with adjustable solubility suitable for printing applications.

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubon S V and Firsov A A 2005 *Nature* **438** 197

[2] Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stormer H L, Zeitler U, Mann J C, Boebinger G S, Kim P and Geim A K 2007 *Science* **315** 1379

[3] Dresselhaus M S and Araujo P T 2010 *ACS Nano* **4** 6297

[4] Geim A and Novoselov K 2007 *Nat. Mater.* **6** 183

[5] Hernandez Y *et al* 2008 *Nat. Nanotechnol.* **3** 563

[6] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666

[7] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y and Hong B H 2009 *Nature* **457** 706

[8] Reina A, Jia X T, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 *Nano Lett.* **9** 30

[9] Berger C *et al* 2006 *Science* **312** 1191

[10] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 *Nature* **442** 282

[11] Eda G and Chhowalla M 2010 *Adv. Mater.* **22** 2392

[12] Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S T and Ruoff R S 2007 *Carbon* **45** 1558

[13] Eda G, Fanchini G and Chhowalla M 2008 *Nat. Nanotechnol.* **3** 270

[14] Lotya M, King P J, Khan U, De S and Coleman J N 2010 *ACS Nano* **4** 3155

[15] Si Y and Samulski E T 2008 *Nano Lett.* **8** 1679

[16] Yoo E J, Kim J, Hosono E, Zhou H S, Kudo T and Honma I 2008 *Nano Lett.* **8** 2277

[17] Miller J M, Dunn B, Tran T D and Pekala R W 1999 *Langmuir* **15** 799

[18] Lin Y M, Jenkins K A, Valdes-Garcia A, Small J P, Farmer D B and Avouris P 2009 *Nano Lett.* **9** 422

[19] Williams J R, DiCarlo L and Marcus C M 2007 *Science* **317** 638

[20] Shin Y J, Wang Y Y, Huang H, Kalon G, Wee A T S, Shen Z, Bhatia C S and Yang H 2010 *Langmuir* **26** 3798

[21] Yang H, Shan C, Li F, Han D, Zhang Q and Niu L 2009 *Chem. Commun.* 3880