# Direct exfoliation of graphite using a non-ionic polymer surfactant for fabrication of transparent and conductive graphene films†

Min Soo Kang,[a] Kyung Tae Kim,[a] Jea Uk Lee[b] and Won Ho Jo*[a]

A high-yielding dispersion of graphene at high concentration in solvent is critical for practical applications. Herein, we demonstrate the formation of a stable dispersion of pristine graphene in ethanol by exfoliating graphite flakes into individual graphene layers using a non-ionic polymer surfactant under bath-type sonication. Oligothiophene-terminated poly(ethylene glycol) was synthesized and used as a non-ionic and amphiphilic surfactant for exfoliating graphite into graphene. A high-quality graphene film was fabricated from the exfoliated graphene solution by the vacuum filtration method. TEM and SEM reveal that the size of exfoliated graphene flakes is larger than 1 μm. When the graphene film was treated with nitric acid and thionyl chloride after washing with solvent, the film showed high performance with a sheet resistance of 0.3 kΩ sq$^{-1}$ and a transparency of 74% at 550 nm.

## Introduction

Transparent and electrically conductive electrodes have been an essential part for organic electronics such as organic light-emitting diodes and organic photovoltaics. Recently, due to its unique physical properties such as room temperature quantum effect, ambipolar electric field effect and high charge carrier mobility, graphene has attracted great attraction from both academia and industry as a transparent and electrically conductive electrode material.[1,2] For these advantages of graphene to be realized in practical applications, it is essential to develop a high-yield and high throughput method for fabrication of graphene. The approaches to fabricate graphene are categorized into two methods: (1) top-down exfoliation of graphite into graphene by breaking π-bonding between graphite sheets[3–7] and (2) bottom-up formation of sp$^2$-bonding between carbon atoms in a monolayer.[8–13] The first method includes mechanical and chemical exfoliation of graphite and the second one includes chemical vapor deposition (CVD) and epitaxial growth on silicon carbide. Though recent works based on the CVD method using catalytic metal substrates have shown the possibility to grow a large-area graphene layer and thereby fabricate a highly transparent and flexible conducting electrode,[14] the production cost is very high due to the expensive substrate and the high-temperature process.

Chemical exfoliation methods based on the Hummers' method,[15] oxidation of graphite to produce graphene oxide (GO) followed by chemical or thermal reduction, have an advantage of potentially low-cost and solution-processed fabrication.[16–18] However, the reduction process may not completely recover graphene from GO containing a substantial amount of structural defects such as carboxylic acid, carbonyl, hydroxyl and epoxide groups, which degrade the electrical properties of graphene: the reported sheet resistance obtained from the reduced GO film ranges from 1 to 70 kΩ sq$^{-1}$ (<80% transmittance) or from 31 kΩ sq$^{-1}$ to 19 MΩ sq$^{-1}$ (at 95% transmittance), which is much higher than that of ITO.[19–21] Although several other top-down methods for preparation of stable suspension of graphene have been reported, including the direct dispersion of graphite in organic solvents such as N-methyl-2-pyrrolidone,[22] dimethylformamide[23] and o-dichlorobenzene,[24] the graphene yield by those methods is very low. The dispersion of graphene by ionic polymer surfactants has recently been reported.[25,26] However, the resulting graphene films do not exhibit impressive conductivity because the interaction between the graphene sheet and the ionic surfactant is not so strong as to fully exfoliate graphite flakes.

In our previous work,[27] we synthesized a non-ionic surfactant composed of oligothiophene and polyethylene glycol (PEG), and used a surfactant to disperse single-walled carbon nanotubes (SWCNTs) in aqueous media for fabrication of highly conductive and transparent thin films. Since the oligothiophene part in the surfactant is absorbed on the SWCNT surface due to π–π interaction between thiophene and CNTs, and PEG is soluble in ethanol, the surfactant easily disperses SWCNTs in ethanol.

[a]Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea. E-mail: whjpoly@snu.ac.kr

[b]Composite Materials Research Group, Korea Institute of Materials Science, Changwon, Gyeongnam, 642-831, Korea

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Hence, it is expected that this concept can also be applied to exfoliation and dispersion of graphene layers from graphite in organic media. Other groups have recently used various types of surfactants for exfoliation of graphite,[28–30] but the conductivities of graphene films are not satisfactory. In this paper, we report the fabrication of highly conductive and transparent graphene films from graphite by using quinquethiophene-terminated PEG (5TN-PEG) as a surfactant. This method has an important advantage over other top-down exfoliation methods, because this method does not require an extra process for exfoliation of graphite while other methods such as the oxidation–reduction method need extra chemical processes. When the film fabricated by our method was treated with nitric acid and thionyl chloride after the 5TN-PEG surfactant was removed by washing with THF during vacuum filtration, the film exhibited a very low sheet resistance of 0.3 $k\Omega$ $sq^{-1}$ with 73% transmittance at 550 nm. This value is the lowest sheet resistance among graphene films prepared by the top-down fabrication of graphene to the best of our knowledge.

## Experimental

### Materials

Graphite flakes were purchased from Sigma Aldrich and used without further purification. Quinquethiophene-terminated poly(ethylene glycol) (5TN-PEG) ($M_w$ of PEG = 2000 g $mol^{-1}$) was synthesized according to our previous report.[27]

### Preparation of graphene solution

To exfoliate graphite into graphene in ethanol, graphite flakes (5.2 mg) and 5TN-PEG (52 mg) were added in 10 mL of ethanol, and the solution was stirred for 5 h. The graphene solution was then sonicated in a bath-type sonicator (Hwashin Instrument, Power Sonic 410) for 5 h and then centrifuged at 2000 rpm for 90 min. The supernatant was carefully decanted and diluted with 1 L of ethanol.

### Fabrication of graphene film

The graphene solutions of 0.01, 0.05 and 0.09 mL were diluted with ethanol to control the thickness of graphene films. During vacuum filtration, the film was rinsed sequentially with ethanol, methanol, THF, DMSO and DMF. After the graphene films deposited on alumina oxide (AAO) film were annealed at 60 °C for 5 h, the films were floated on 3 M NaOH aqueous solution while AAO is dissolved. Water was added to solution until the pH of solution reached 7, and then the residual solution was imbibed completely to transfer graphene film to the glass substrate. The film was dried in air for 2 h and then annealed at 120 °C for 5 min. Finally, films were chemically treated with $HNO_3$ (60%) and $SOCl_2$ (>99%) for hole doping and/or removal of residual surfactant by dipping the films in $HNO_3$ (60%) for 3 h and drying in air followed by dipping in $SOCl_2$ for 3 h and drying in air.

### Characterization and measurement

The transmittance of graphene film was measured using a UV-visible spectrophotometer (HP 8452A). The morphology of graphene film was observed using a transmission electron microscope (JEOL, JEM-1010). Electrical property of graphene film was characterized by a four-point probe measurement system (Napson, CRESBOX). The chemical structure of graphene film was analyzed using a FT-IR spectrometer (Thermo Scientific, Nicolet 6700). Fluorescence spectra were obtained on a fluorescence spectrometer (RF 5301, Shimadzu). X-ray photoelectron spectra were obtained on an AXIS-His (Kratos). The film thickness was measured by AFM (Surface imaging system, NS4A).

## Results and discussion

### Exfoliation and dispersion of graphene

One of the goals of this work is to prepare a homogeneous dispersion of graphene in solution directly from graphite using a polymeric surfactant (5TN-PEG) whose chemical structure is shown in Fig. 1a. It has been known that the oligothiophene part (5TN) in 5TN-PEG is strongly physisorbed onto the graphene surface *via* strong $\pi$–$\pi$ interaction[31] while PEG is soluble in ethanol, THF and other various solvents. Among the organic solvents tested, ethanol was the best solvent to disperse SWCNTs in the presence of 5TN-PEG in the previous study.[32]

When the graphite is exfoliated and dispersed in various organic solvents using 5TN-PEG as a surfactant, as shown in Fig. 1b, it is realized that graphite is well exfoliated and dispersed in ethanol while graphite is not dispersed in THF. It should be noted here that the color of graphite–5TN-PEG solution in THF is reddish purple, indicating that THF selectively dissolves the surfactant, 5TN-PEG.

When the UV-vis absorption spectrum of graphite–5TN-PEG in ethanol is compared with that of THF solution, as shown in
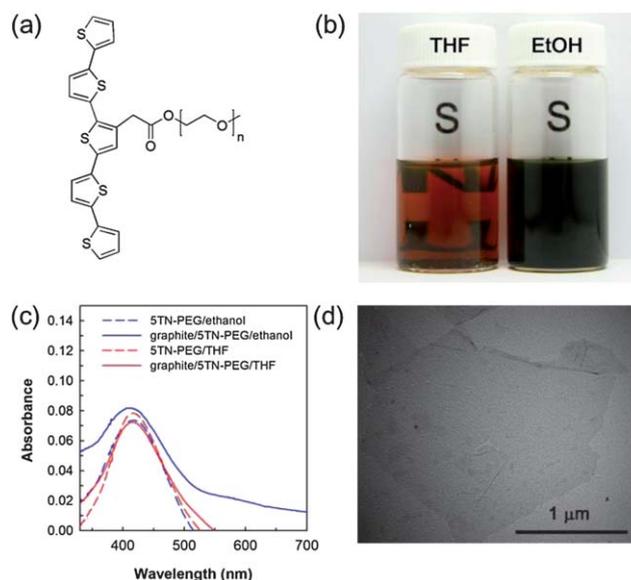


**Fig. 1** (a) Chemical structure of 5TN-PEG; (b) comparison of graphite–5TN-PEG in THF and ethanol; (c) UV-vis absorption spectra of 5TN-PEG–ethanol (dashed blue) and graphite–5TN-PEG–ethanol (solid blue), 5TN-PEG–THF (dashed red), and graphite–5TN-PEG–THF (solid red); (d) TEM image of exfoliated graphene.

Fig. 1c, the graphite–5TN-PEG in ethanol shows a wide range absorption of graphene (500–700 nm) with an absorption peak at 410 nm corresponding to the absorption of 5TN,[33] whereas the graphite–5TN-PEG in THF does not show the wide absorption of graphene, indicating that graphite is not exfoliated in THF. The poor exfoliation and dispersibility of graphene in THF is presumably because both 5TN and PEG are very soluble in THF, while ethanol cannot dissolve 5TN which allows the 5TN to interact with the graphene surface by $\pi$–$\pi$ interaction. The interaction between 5TN and graphene is further evidenced by fluorescence emission spectroscopy. The emission intensity of 5TN-PEG is decreased in ethanol solution of graphene–5TN-PEG due to interaction between 5TN and graphene, while the emission intensity of graphene–5TN-PEG in THF shows almost the same intensity as that of pure 5TN-PEG solution (see Fig. S1, ESI†). Therefore, THF is not a proper solvent for exfoliation and dispersion of graphite, but it would be rather a good solvent for washing out excess 5TN-PEG physisorbed on the graphene surface after fabrication of graphene film. When we used pyrene butyric acid (PBA)[26] as a surfactant for comparison with 5TN-PEG, the emission intensity of PBA in ethanol and THF was almost the same as graphene–PBA in ethanol and THF (see Fig. S2, ESI†), indicating that PBA cannot disperse graphene in ethanol.

The transmission electron microscopy (TEM) image of graphene sheets dispersed in ethanol shows that graphene sheets with the size larger than 1 µm are homogeneously dispersed in ethanol by 5TN-PEG (Fig. 1d).

## Fabrication of graphene film

Various methods for solution-based graphene deposition including vacuum filtration (VF),[34] spraying,[23] dip coating[35] and spin coating[36] have been reported. To prepare a highly transparent graphene film, we used the vacuum filtration method because of the ease of transfer, thickness control, solvent treatment, and uniformity of the film.

Surfactant removal is an important step for fabrication of a highly conductive graphene film, because the surfactant adsorbed on the graphene surface prevents charge carrier transport through graphene layers.[37] UV-vis spectra of graphene films washed with various solvents were measured and compared to identify the removal of surfactant.

The film washed with ethanol still has a strong absorption in the range of 400–550 nm due to the absorption of 5TN, while the absorptions of the films washed with other solvents are relatively weak, as shown in Fig. 2. The transmittances of films at 470 nm corresponding to the maximum absorption of 5TN are listed with the corresponding sheet resistances in Table 1. The film washed with THF has a transmittance of 90.3% at 470 nm while the film washed with ethanol exhibits a transmittance of 68.1%. Furthermore, the film washed with THF has a lower sheet resistance (19 kΩ sq$^{-1}$) than other films. These results suggest that THF is the most suitable solvent for washing 5TN-PEG from graphene film to prepare a highly conductive and transparent graphene film. When the infrared spectrum of the as-prepared graphene–5TN-PEG film was compared with that of the graphene film washed with THF (see Fig. S3, ESI†), the
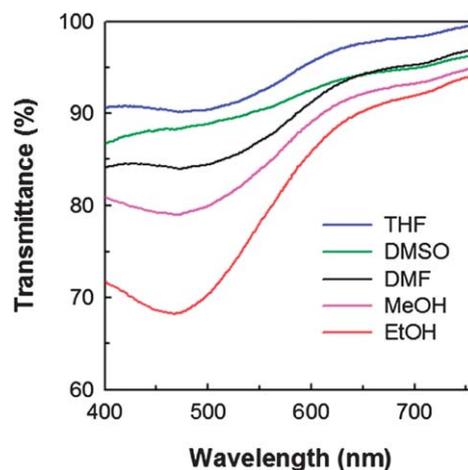


**Fig. 2** Transmittance spectra of graphene films washed with various solvents.

**Table 1** Transmittance at 470 nm and sheet resistance of films washed with various solvents

| Solvent | Transmittance at 470 nm (%) | Sheet resistance (kΩ sq$^{-1}$) |
|---|---|---|
| Ethanol | 68.1 | 76 |
| Methanol | 79.2 | 30 |
| DMSO | 88.3 | 21 |
| DMF | 83.9 | 26 |
| THF | 90.3 | 19 |

spectrum of THF-washed film shows a characteristic peak of graphene at 1600 cm$^{-1}$,[38] but does not show characteristic peaks of 5TN-PEG (2880 and 1280–1210 cm$^{-1}$, C–H stretching; 1730 cm$^{-1}$, ester C═O stretching; 1072 cm$^{-1}$, C–S stretching; 713 cm$^{-1}$, ═C–H bending of thiophene),[39,40] indicating that most of 5TN-PEG was removed after washing with THF.

## Chemical treatment of graphene film

For the purpose of enhancing the electrical and optical properties of graphene films, the washed graphene films are further treated with HNO$_3$ and SOCl$_2$. The color of graphene film changes from reddish to gray on treatment with both HNO$_3$ and SOCl$_2$ (inset of Fig. 3a). When the UV-vis spectra of graphene films are compared before and after acid treatment (Fig. 3a), the transmittance at 470 nm corresponding to the absorption peak of 5TN-PEG is increased from 90.1% to 95.4% after HNO$_3$/SOCl$_2$ treatment, indicating that the residual 5TN-PEG surfactant was removed by HNO$_3$/SOCl$_2$ treatment. It should be noted here that the thiophene ring can easily be decomposed into sulfur and trioxide by nitric acid.[41]

When the sheet resistance of graphene film is plotted against the transmittance, as shown in Fig. 3b and Fig. S4 (ESI†), it is found that the HNO$_3$/SOCl$_2$ treatment not only increases the transmittance but also significantly reduces the sheet resistance of graphene film. The graphene film with 73% transmittance at 550 nm has a low sheet resistance of 0.3 kΩ sq$^{-1}$ after HNO$_3$/SOCl$_2$ treatment, which is lower by one order of
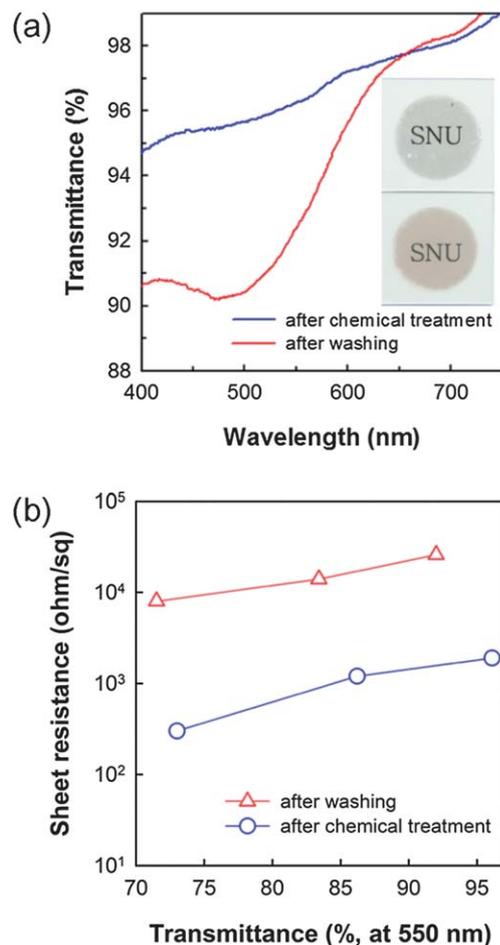
**Fig. 3** (a) Transmittance of graphene films before and after chemical treatment, where the inset shows the visual transparency of graphene films with a transmittance of 80% at 650 nm deposited on 25 mm × 25 mm bare glass after washing (lower one) and after chemical treatment (upper one); (b) plot of the sheet resistance of graphene film as a function of the transmittance at 550 nm.
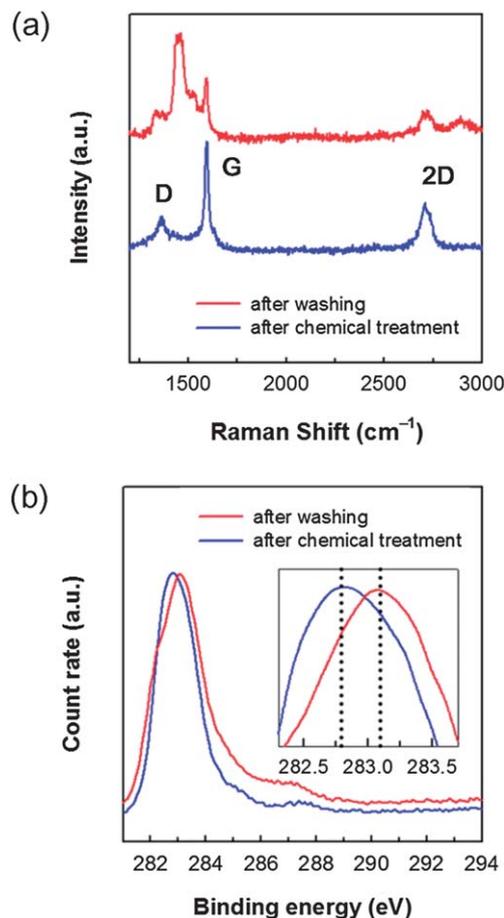


**Fig. 4** (a) Comparison of the Raman spectrum of graphene film after washing with its spectrum after chemical treatment and (b) XPS spectra of C 1s of graphene after washing (red) and chemical treatment (blue).

magnitude as compared with the graphene film washed only with THF. It has been reported that the $HNO_3/SOCl_2$ treatment of graphene enhances the electrical conductivity by the doping effect of $HNO_3$ and $SOCl_2$.[42–44]

Fig. 4a shows comparison of the Raman spectrum of the washed graphene film with that of the $HNO_3/SOCl_2$ treated film. The Raman spectrum of acid treated film shows only characteristic peaks of graphene, G peak at ~1580 cm$^{-1}$, D peak at ~1350 cm$^{-1}$ and 2D peak at ~2700 cm$^{-1}$, while the spectrum of washed film exhibits additional peaks at 1450–1530 cm$^{-1}$ and 2900 cm$^{-1}$ corresponding to thiophene ring stretching and C–H stretching, respectively, indicating that residual 5TN-PEG was successfully removed by the $HNO_3/SOCl_2$ treatment.

Analysis of 2D peak in the Raman spectrum is an accepted method to estimate the number of graphene layers.[45] It has recently been proposed that the number of graphene layers increases as the intensity ratio of G peak to 2D peak ($I_G/I_{2D}$) increases: the values of $I_G/I_{2D}$ for bilayer graphene and trilayer graphene are about 2.2–3.5 and 3.5–4.5, respectively.[46] The intensity ratio of our graphene film is smaller than 2.5 (Fig. 4a), indicating that our film has 2–3 graphene layers. The number of

graphene layers can be directly counted from a high-resolution TEM image. The TEM image of randomly imaged graphene edge shows 2 layers (see Fig. S5, ESI†), which is very consistent with the above result. The atomic force microscopy (AFM) image also shows a thickness of 1.14 nm, corresponding to the thickness of bilayer or trilayer graphene (Fig. S6, ESI†).

It has been known that another intensity ratio of D to G peak ($I_D/I_G$) is related to the crystalline quality of graphene layers: the smaller the value, the better the crystalline quality. The $I_D/I_G$ value of our graphene film is below 0.35, which is much smaller than those of reduced graphene oxide (>0.8)[47] and other graphene films fabricated via the intercalation method,[34] indicating that the graphene layers directly exfoliated from graphite flakes using 5TN-PEG as a surfactant have much less defects and thus exhibit better electrical properties as compared to those prepared by other methods.

The effect of chemical treatment on the electrical property of graphene film was also examined by X-ray photoelectron spectroscopy (XPS) (Fig. 4b). The C 1s peak at 283.1 eV for graphene film was downshifted to 282.8 eV after the $HNO_3/SOCl_2$ treatment, providing an evidence for p-type doping by the chemical treatment.[14,48] The p-doping is expected to enhance the electron mobility, which results in lowering of the sheet resistance.

## Comparison of electro-optical property of our graphene film with other works reported in the literature

Fig. 5 and Table 2 compare our result with other data reported for electro-optical properties of graphene films. Our graphene film prepared by direct exfoliation of graphite flakes shows a better electro-optical performance than most of other films. Although Li and his co-workers[49] have reported an excellent performance of 657 $\Omega$ sq$^{-1}$ sheet resistance with 96% transmittance at 550 nm, they fabricated graphene films through a complicated procedure of electro-chemical exfoliation of graphite in sulfuric acid, while our method to exfoliate graphite and to disperse graphene in solvent is simpler, cheaper and more convenient.

The two most important factors to evaluate the performance of transparent electrode are the sheet resistance and transparency. However, it is not always easy to compare these two parameters at a glance because the sheet resistance of graphene film is strongly correlated with the transparency. Hence, it has recently been proposed that the ratio of direct current conductivity ($\sigma_{dc}$) to the optical conductivity ($\sigma_{ac}$) (at typically 550 nm) can be used as a figure of merit for electro-optical property of graphene film,[50,51] where a higher value of $\sigma_{dc}/\sigma_{ac}$ indicates a better electro-optical performance of graphene film. When the $\sigma_{dc}/\sigma_{ac}$ value of our film is compared with those of other groups,

**Table 2** Comparison of electro-optical performance of our graphene film with other films reported in the literature

| Source of graphene | Surfactant | Method | Treatment | $\sigma_{dc}/\sigma_{ac}$ |
|---|---|---|---|---|
| GO | None | SC$^c$/HR$^d$ | 1100 °C thermal annealing | 0.38 (ref. 53) |
| GO | SDS$^a$ | VF$^e$ | HNO$_3$/SOBr$_2$ | 1.12 (ref. 42) |
| GO | None | SC$^c$/HR$^d$ | 400 °C thermal annealing | 1.75 (ref. 19) |
| Graphite | H$_2$SO$_4$ | EC$^f$/DC$^g$ | HNO$_3$ | 13.9 (ref. 49) |
| Graphite | None | SP$^h$ | 250 °C thermal annealing | 0.67 (ref. 23) |
| Graphite | SDBS$^b$ | VF$^e$ | HNO$_3$ | 1.22 (ref. 52) |
| Graphite | 5TN-PEG | VF$^e$ | HNO$_3$/SOCl$_2$ | 3.65 |

$^a$ Sodium dodecyl sulfate. $^b$ Sodium dodecyl benzene sulfonate. $^c$ Spin coating. $^d$ Hydrazine vapor reduction. $^e$ Vacuum filtration. $^f$ Electrochemical exfoliation. $^g$ Drop casting. $^h$ Spray coating.

our film has a much higher value than other graphene films, indicating that our graphene film shows better optical and electrical performance than other graphene films.

## Conclusions

We have successfully exfoliated graphite directly into graphene layers by using a non-ionic surfactant, quinquethiophene-terminated poly(ethylene glycol) and dispersed homogeneously the layers in ethanol. A high electro-optical graphene film was fabricated from the graphene dispersion by vacuum filtration. After washing the surfactant with THF followed by chemical treatment with HNO$_3$ and SOCl$_2$, the graphene film exhibited high performance (a transmittance of 74% at 550 nm, a sheet resistance of 0.3 k$\Omega$ sq$^{-1}$ and $\sigma_{dc}/\sigma_{ac}$ = 3.65). These results lead us to conclude that the direct exfoliation of graphite into graphene layers by the use of a proper surfactant has a strong potential for fabrication of highly transparent and conductive graphene films.

## Acknowledgements

**Fig. 5** (a) Comparison of electro-optical property of our film with those of graphene films reported by other groups and (b) figure of merit values of our film and graphene films reported by other groups.

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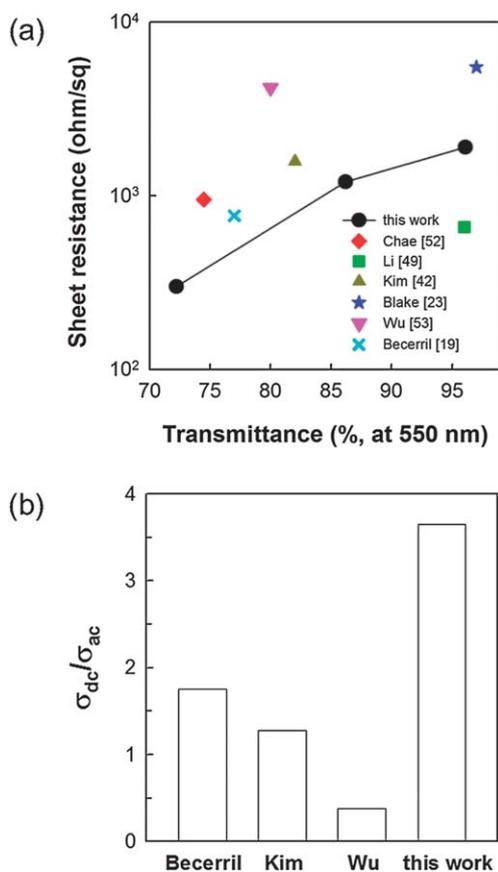5 S. Park and R. S. Ruoff, *Nat. Nanotechnol.*, 2009, **4**, 217–224.

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