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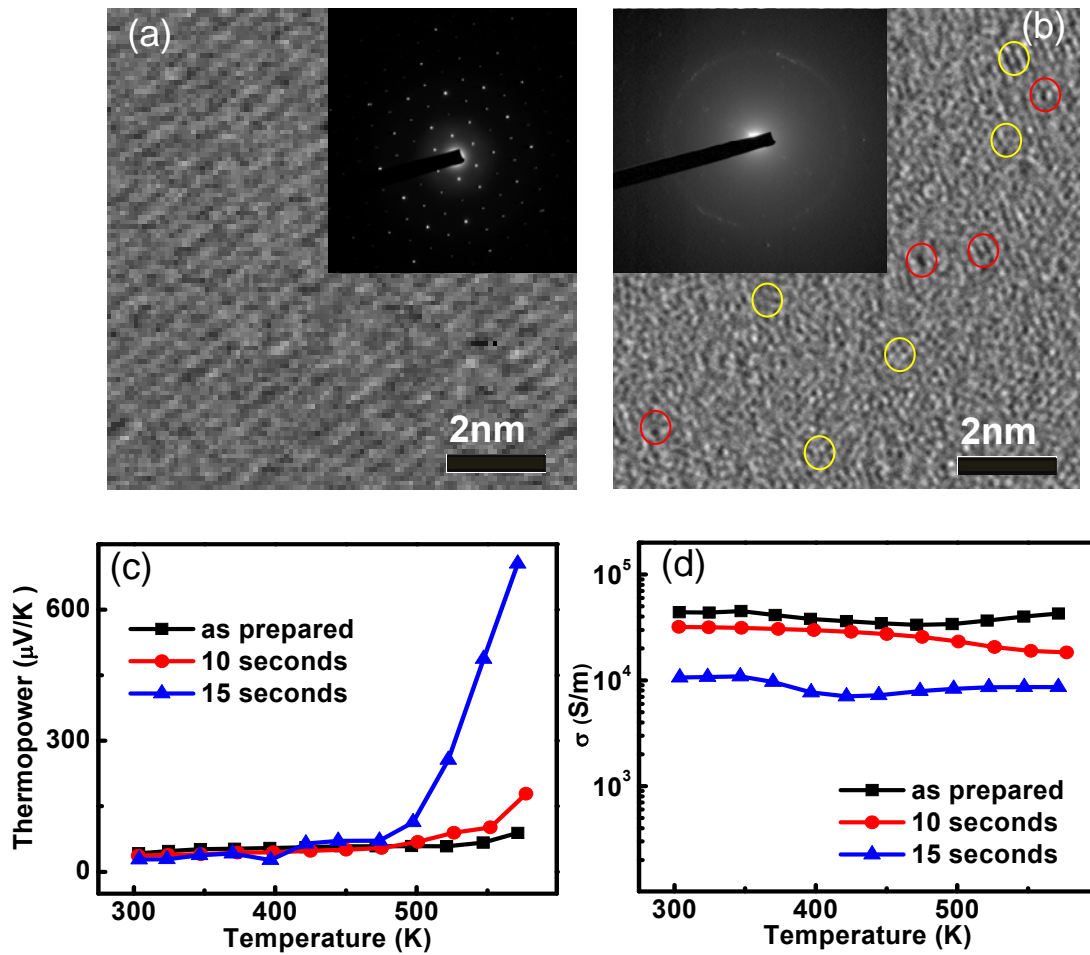
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Enhanced Thermopower of Graphene Films with Oxygen Plasma Treatment

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Abstract

In this work, we show that the maximum thermopower of few layers graphene (FLG) films could be greatly enhanced up to $\sim 700\mu\text{V/K}$ after oxygen plasma treatment. The electrical conductivities of these plasma treated FLG films remain high, *e.g.* $\sim 10^4\text{S/m}$, which results in power factors as high as $\sim 4.9 \times 10^{-3}\text{ W K}^{-2}\text{m}^{-1}$. In comparison, the pristine FLG films show a maximum thermopower of $\sim 80\mu\text{V/K}$ with electrical conductivity of $\sim 5 \times 10^4\text{ S/m}$. The proposed mechanism is due to generation of local disordered carbon that opens the band gap. Measured thermopowers of single-layer graphene (SLG) films and reduced graphene oxide (rGO) films were in the range of $-40\sim 50$ and $-10\sim 20\mu\text{V/K}$, respectively. However, such oxygen plasma treatment is not suitable for SLG and rGO films. The SLG films were easily destroyed during the treatment while the electrical conductivity of rGO films is too low, which makes FLG films unique for possible TE applications.

Keywords: graphene film, oxygen plasma, thermopower

Introduction

Graphene,¹ the one atomic sp^2 -bonded planar carbon sheet, has inspired considerable research in its fundamental intrinsic properties^{2,3} and its potential applications in sensor,⁴⁻⁹ transistor¹⁰⁻¹³ and solar cell.¹⁴⁻¹⁶ Recently, the thermoelectric property of graphene became a hot research topic¹⁷⁻²⁴ due to its promising applications. Previous theoretical work on graphene demonstrated that the calculated thermoelectric figure of merit,¹⁷⁻¹⁹ ZT , could be tuned to be as high as above 4.^{20, 21}

Here, ZT is formulated as $ZT = \frac{S^2 \sigma}{\kappa}$, where S , σ , κ and T are the thermopower (or Seebeck coefficient), electrical conductivity, thermal conductivity and temperature in Kelvin, respectively.

However, the experimental results of the thermoelectric property of graphene or carbon nanotubes (CNTs) are not promising,²²⁻²⁴ *e.g.* ZT is normally in the order of $\sim 10^{-2}$. The main factors causing such low ZT values are the high thermal conductivity (lattice thermal conductivity) of graphene/ CNTs, and the extremely low thermopower, *e.g.* typically in the range of $30\text{-}80\mu\text{V/K}$.^{20, 22, 23, 25, 26} In the former case, although the pristine graphene/CNTs are well known to possess high thermal conductivities,²⁷⁻³⁰ there are reports on experimental and theoretical approaches^{20, 24, 31-35} to reduce the thermal conductivity of processed graphene/CNTs through structural defect generation and controlling the roughness of the graphene edge. For example, the phonon thermal transmission could be suppressed orders of magnitude by increasing the degree of disorder.²¹ For the latter issue, however, not much improvement has been developed. The reported maximum thermopower of graphene/CNTs is only $\sim 80\mu\text{V/K}$.³⁶ Developing an engineering process that can significantly increase the thermopower without degrading the high electrical conductivity of graphene may be useful to open up the possibility for applications in thermoelectric energy conversion or thermal sensors.

Here, we report the study on the temperature-dependent thermopower of few layers graphene (FLG) films before and after oxygen plasma treatment. We found that the maximum thermopower of the pristine FLG was $\sim 80\mu\text{V/K}$ in the temperature range 475 to 575K with electrical conductivity of $\sim 5 \times 10^4 \text{S/m}$. After oxygen plasma treatment, the maximum thermopower for the same sample could be greatly enhanced up to $\sim 700\mu\text{V/K}$ in the temperature range 475 to 575K while the electrical conductivity maintained in the same order of magnitude $\sim 10^4 \text{S/m}$, which resulted in power factor as high as $\sim 4.9 \times 10^{-3} \text{W K}^{-2} \text{m}^{-1}$. This corresponded to an

increase in the power factor of 15 times higher for oxygen plasma treated FLG films. We also investigated the thermoelectric properties of single layer graphene (SLG) films and reduced graphene oxide (rGO) films, and their corresponding thermopower values were in the range of -40~50 and -10~20 μ V/K, respectively. However, the oxygen plasma treatment was not suitable for SLG and rGO films. The oxygen plasma treatment was very difficult to control for SLG films, which were destroyed easily during the process. For rGO films, the electrical conductivity was too low and the oxygen plasma treatment would further decrease it, which was not ideal to achieve high power factor. This made the FLG films unique for possible TE applications. We proposed that oxygen plasma induced structural disorder could cause the opening of band gap³⁷⁻⁴² leading to the enhancement of the thermopower of FLG films.

Results and discussion

The morphology of the as-prepared graphene films was characterized by optical microscopy and scanning electron microscope (SEM) after being transferred onto SiO₂ (300 nm)/Si substrates. Figure 1a-d shows the optical images and SEM images of SLG films and FLG films respectively. The different color contrast between the graphene films and the SiO₂/Si substrate can be clearly observed, indicating the different thicknesses of the two films. In addition, these optical images display that these graphene films are pretty continuous and fairly uniform up to a long range. Wrinkles are observed in these films, which could come from the thermal stresses created during the cooling process of the substrate after growth as there is a large difference of thermal expansion coefficients for Cu and graphene.⁴³ The AFM images and the height profiles of SLG and FLG films (see Fig. S2 in the Supporting Information) reveal the thickness of these two graphene films are around 1nm for SLG films and 6nm for FLG films respectively. Figure 1e shows the typical Raman spectra obtained from the graphene films. The second-order Raman band located at 2650 cm⁻¹ (2D peak) can be used to indicate the number of layers of graphene films by comparing its relative intensity with respect to that of the G peak located at 1680 cm⁻¹.⁴⁴ As shown by the bottom spectrum in Fig. 1e, the intensity of the 2D peak is about twice of that of the G peak, signifying that the graphene films are only one or two layers. For the top spectrum in Fig. 1e, the intensity of the 2D peak is much lower than that of the G peak, which suggests

that the samples are multilayered. Meanwhile, the D peak at 1350 cm^{-1} is also observed in Fig. 1e for the spectra of both SLG and FLG films. The intensity ratio between the D peak and the G peak, $I(D)/I(G)$, is higher for the FLG films than that of SLG films, which suggests more structural defects in the FLG films.

The thermoelectrical properties of these graphene films were investigated after they were transferred onto glass substrates by using the commercially available ZEM-3 system. The temperature-dependent thermopowers and the corresponding electrical conductivities for the SLG and FLG films are presented in Fig. 2. Due to the delicate structure and high sensitivity of graphene films to environmental factors, the measurement temperatures were set up to 520K for SLG films and 575K for FLG films. The thermopowers of FLG films are p-type with '+' signs in the range of $40\text{-}80\text{ }\mu\text{V/K}$ at temperature between 300 K and 575 K. The maximum thermopower obtained on FLG films at 575 K is comparable to the highest reported values of thermopower of graphene samples³⁶. The thermopowers of SLG films are in the narrow range of $-40\text{-}50\mu\text{V/K}$ and change from '+' to '-' (n-type) at 440 K. The p-type characteristics of SLG films at low temperature, *e.g.* from 300 K to 440K, suggest that holes are the dominant carriers due to the easily adsorbed molecules (*e.g.* oxygen or water) on the surface of SLG films.⁴⁵⁻⁴⁷ At increased measurement temperature, desorption of such molecules leads to a decrease of holes concentration in the SLG films, which results in comparable concentration of both charge carriers. In this case, the sign of the thermopower is determined by the mobility of both the electrons and holes.⁴⁸ The transition of the thermopower of SLG films from '+' to '-' at 440K indicates that the mobility of electrons is higher than that of the holes above this temperature, which makes electrons become the dominant carriers. For the FLG films, there is no such sign change of the thermopower upon increasing the measurement temperature, which suggests holes are still the dominant charge carrier.

The electrical conductivity measurements by four-point probe using ZEM-3 show that the electrical conductivities of SLG films are in the range of $\sim 4\times 10^4\text{-}\sim 6\times 10^4\text{ S/m}$, which is slightly higher than that of the FLG films, *e.g.* $\sim 4\times 10^4\text{-}\sim 5\times 10^4\text{ S/m}$. As indicated from both the Raman spectra and thermoelectric results, the FLG films with a higher density of structural defects show a little higher thermopower as compared to that of the SLG films. It is therefore of interest to intentionally create more structural defects in the samples to investigate their thermoelectric

properties. Here, we used oxygen plasma to treat the FLG films for different duration (10, 15 and 20 seconds) to create different extents of structural disorder in the samples.⁴⁹

The morphology and atomic structure of the FLG films before and after plasma treatment were investigated with high resolution transmission electron microscopy (HRTEM) analysis. Figure 3a exhibits a HRTEM image of pristine FLG film, which shows an ordered lattice structure with a hexagonal symmetric point pattern as revealed by the selected area electron diffraction (SAED, inset in Fig. 3a) analysis. The HRTEM image of plasma treated FLG film in Fig. 3b reveals the relatively disordered lattice structure. The yellow circles highlight small crystals of carbon in such film while the red circles point out the disordered arrangement of carbon atoms. The SAED analysis (see inset in Fig. 3b) showed diffused rings indicated no long range ordering of the carbon atoms. Fig. 3c depicts the Raman spectra of these FLG films with different oxygen plasma treatment durations. It is observed that $I(D)/I(G)$ increases from 0.4 to 1.0 when the oxygen plasma treatment duration increases from 10 seconds to 15 seconds, indicating the increased density of structural defects. For FLG films after plasma treatment for 20 seconds, it is found that the D, G, 2D peaks become broader and less distinguishable indicating that the ordered structure of the FLG films is damaged.

The thermopowers and electrical conductivities of these oxygen plasma treated FLG films are shown in Fig. 3d-e. After 10 seconds treatment with oxygen plasma, the maximum thermopower of the FLG films within the measurement temperature range increases to $170\mu\text{V/K}$ at 575 K as compared to $80\mu\text{V/K}$ for pristine FLG films. Meanwhile, the electrical conductivity of the FLG films decreases by about $\sim 30\%$ to $\sim 2 \times 10^4$ - $\sim 3 \times 10^4$ S/m after such treatment process. Further increasing the treatment time to 15 seconds, we found that the maximum thermopower can be increased to $\sim 700\mu\text{V/K}$ at 575K while the electrical conductivity be decreased to 0.8×10^4 - 1×10^4 S/m. For FLG films after 20 seconds oxygen plasma treatment, the thermopower measurements could not be carried out as the electrical resistance was above the measurement range. It could be possibly due to (1) significant increase in the structural defects that increased the electrical resistivity of the FLG films or (2) the films became discontinuous after such treatment. Although the oxygen plasma treatment decreases the electrical conductivities of the FLG films, the power factors, denoted as $S^2\sigma$, increase significantly mainly due to the greatly enhanced thermopower, *e.g.* $4.9 \times 10^{-3} \text{ W K}^{-2}\text{m}^{-1}$ and $8.67 \times 10^{-4} \text{ W K}^{-2}\text{m}^{-1}$ for the 10-second and 15-second treated films as

compared to $3.2 \times 10^{-4} \text{ W K}^{-2} \text{ m}^{-1}$ for pristine FLG films. This corresponds to an increase in the power factor of 15 times higher for 15-second oxygen plasma treated FLG films than as for pristine FLG films. We also performed oxygen plasma treatments on the SLG films. However, the process is much more difficult to control and most of the films became insulating after even short duration of treatment.

Besides inducing structural disorder, the oxygen plasma treatment may also generate chemical functional groups, *e.g.* $-\text{OH}$ or $-\text{COOH}$ *etc.*, in the graphene films.⁴⁹ In order to examine the effects of these chemical functional groups on the thermoelectric properties of the graphene films, we further measured the thermopower and electrical conductivities of rGO films on glass substrates produced by Hummers method,⁵⁰ because it is well recognized that various chemical functional groups, *e.g.* $-\text{OH}$ or $-\text{COOH}$ *etc.*, exist in the rGO films.^{12, 51-53}

The Raman spectrum of the rGO films (see Fig. 4a) shows strong D peak with $I(\text{D})/I(\text{G}) = 1.45$, which is much higher than that of chemical vapor deposition (CVD) grown SLG and FLG films. As shown in Fig. 4b, the thermopowers of rGO films are in the range of $-10 \sim 20 \mu\text{V/K}$ with the electrical conductivity of $2 \times 10^3 \sim 9 \times 10^3 \text{ S/m}$. Since this electrical conductivity is already too low to achieve high power factors, we did not carried out oxygen plasma treatment on the rGO films, which may further decrease the electrical conductivity. The power factor calculated for rGO films is in the range of $0.8 \times 10^{-6} \sim 3.6 \times 10^{-6} \text{ W K}^{-2} \text{ m}^{-1}$, which is about three orders of magnitude lower than that of FLG films after 15 seconds oxygen plasma treatment. The above observations indicate that those functional groups in rGO films may not be helpful in enhancing the thermopower. Thus, the significant enhancement in the thermopower of FLG films after oxygen plasma treatment is expected to be directly related to the generation of the structural defects/disorder.

In order to understand the role of oxygen-plasma induced defects on the increase of the thermopower of graphene, we further used Kubo's formula based on the tight-binding model to simulate the thermopower of FLG samples (the details are elaborated in the supporting information). The calculated results show that the band gap in FLG caused by oxygen plasma induced defects through breaking its sublattice equivalence and narrowing the band^{49, 54} can greatly increase the magnitude of the thermopower up to $> 500 \mu\text{V/K}$, similar to our experimental values. However, it is noted that the calculated linear relationship between

thermopower and temperature deviated from the trend of the curves for our experimental results. We attributed this deviation to the strong impurity scattering in FLG films.

Conclusions

In summary, we measured the thermopower of FLG films and found the thermopower of the FLG films could be greatly enhanced by oxygen plasma treatment process in the temperature range of 475-575K. After 15 seconds treatment, the maximum thermopower was $\sim 700 \mu\text{V/K}$ at 575 K with electrical conductivity of $\sim 1 \times 10^4 \text{ S/m}$. This resulted in a power factor of $4.9 \times 10^{-3} \text{ W K}^{-2} \text{ m}^{-1}$, which is about 15 times higher than that of pristine FLG films. Further measurements on the rGO films showed very low thermopower. We attributed the greatly enhanced thermopower in the oxygen plasma treated FLG films to the generation of structural disorders, which opened the π - π^* gap.

Experimental section

Preparation of FLG films: FLG films were prepared on $25 \mu\text{m}$ thick Cu foils (purchased from Alfa Aesar) by chemical vapor deposition (CVD) method with ethanol as precursor under atmosphere condition. In a typical growth process, the Cu substrate was heated to 900°C in the CVD chamber with Ar/H₂ (with flow rate of $\sim 1000 \text{ sccm}$). Ethanol was introduced with H₂ flow (100 sccm) into the CVD chamber and the flow was kept at 900°C for 30 minutes. Finally, the Cu foil was cooled down under Ar/H₂ environment. After the growth of CVD graphene films, Cu foils with as-grown graphene films were spin-coated with a thin layer of PMMA (polymethylmethacrylate) and then the samples were immersed into iron nitrate solution to remove the Cu foil. The detached graphene films were transferred to the desired substrates, *e.g.* silicon or glass. After transferring, the PMMA was removed using acetone. Finally the graphene on the desired substrate was washed using DI water and blow-dried gently with N₂ gas.

Preparation of SLG films: SLG film was prepared on $25 \mu\text{m}$ thick Cu foils (purchased from Alfa Aesar) by chemical vapor deposition (CVD) method.⁵⁵ In a typical growth process, the Cu substrate was loaded in the CVD chamber and pumped to vacuum condition (10^{-2} Torr) before Ar/H₂ with flow rate of $\sim 400 \text{ sccm}$ was introduced back into the chamber. Samples were heated to 950°C at a pressure of $\sim 8\text{-}9 \text{ Torr}$. The Ar/H₂ flow was then stopped and the hexane vapor at a

rate of ~4ml/h was introduced into the CVD chamber to keep the pressure of 500mTorr for a few minutes. Finally, the Cu foil was cooled down under Ar/H₂ environment. The Cu foil etching and transfer procedures are the same as that for the FLG films as described above.

Preparation of rGO film: Graphene oxide (GO) sheets were synthesized by a modified Hummer method using natural graphite as reported.⁵⁰ Then, the GO aqueous solution was spin cast onto the glass substrates with thicknesses of ~15 nm. Finally, the GO sheets on glass substrates were reduced by hydrazine to rGO films.

Oxygen plasma treatment of FLG films: The graphene films were treated with the plasma cleaner set consisting of PDC-32G and PDC-FMG plasmaflo (Harrick Plasma, USA). FLG films on glass substrates were directly exposed to plasma cleaner with oxygen/ argon (1:10) mixture gas under low setting (input power~6.8W) for a few seconds.

Characterization: The morphology and structure of graphene films were inspected by optical microscope, atomic force microscopy and Raman spectroscopy. The optical images were obtained using Nikon Eclipse Me 600 microscope. The AFM images were obtained using Dimension 3100 (Veeco, CA, USA) in a tapping mode with a Si tip under ambient conditions. Raman spectra were obtained with a WITec CRM200 confocal Raman microscopy (WITec Instruments Corp, Germany) using a 488 nm exciting radiation. TEM images of the samples were obtained by using transmission electron microscopy (TEM) system (JEOL, Model JEM-2100) operating at 200 kV.

Thermoelectric properties characterization: The thermopower and conductivity of graphene films on glass substrates were measured using a commercial available ZEM-3 Seebeck meter at pre-selected temperature range from 300K to 550K under helium gas environment.

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Supporting Information Available:

Complete model simulation, AFM images and height profiles of FLG and SLG films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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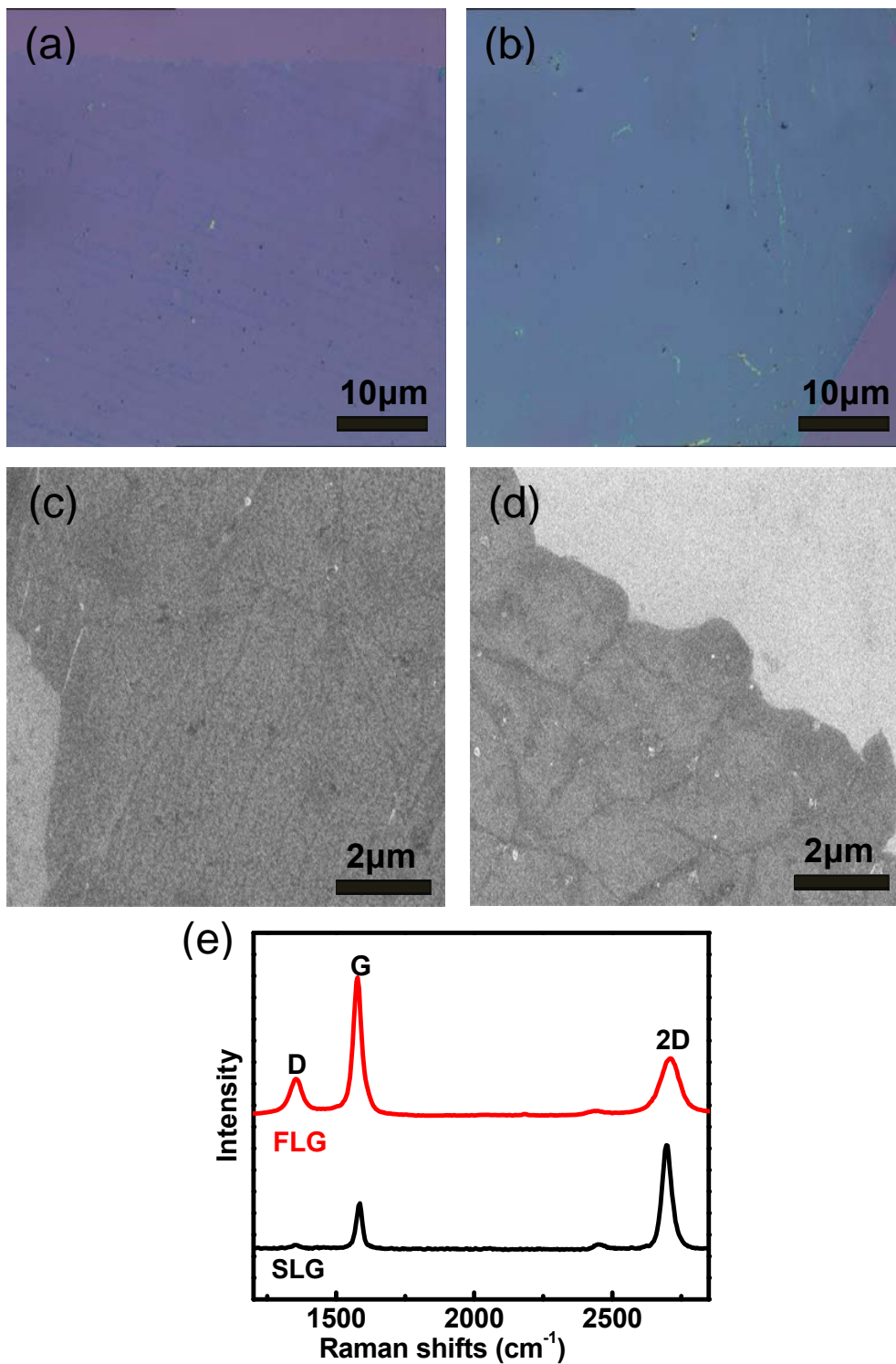


Figure 1. Characteristics of graphene films on SiO₂ (300 nm)/Si substrates. **(a-b)** Optical microscopy images of **(a)** SLG and **(b)** FLG films on SiO₂ (300 nm)/Si substrate. The different contrast between the substrate and graphene film shows the different thicknesses. **(c-d)** SEM images of **(c)** SLG and **(d)** FLG films on SiO₂ (300 nm) /Si substrate. **(e)** the corresponding Raman spectra of the SLG and FLG films.

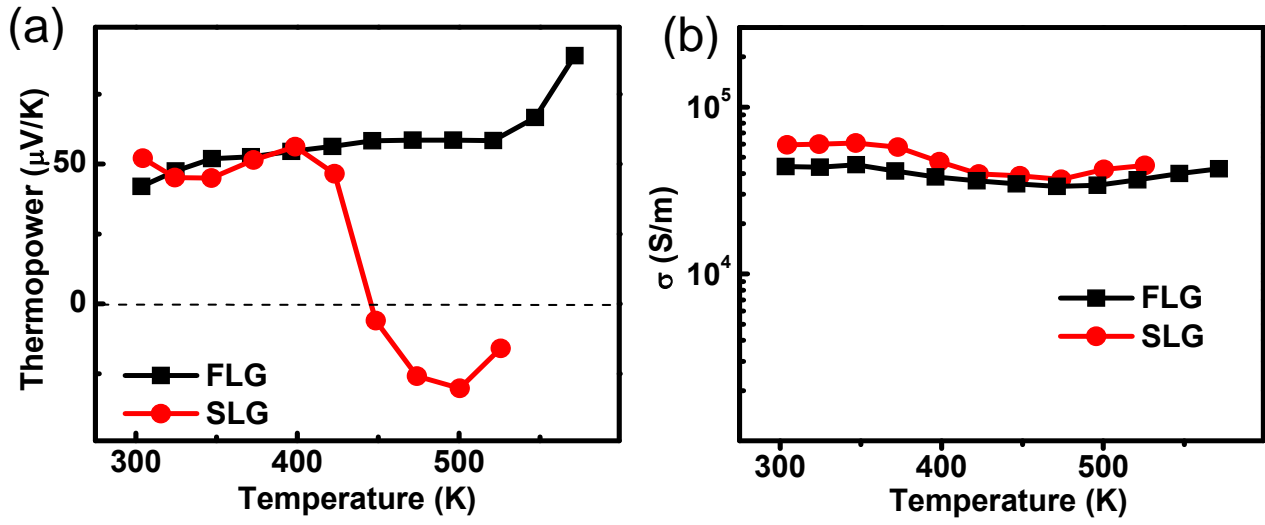


Figure 2. Thermoelectrical properties of graphene films. Temperature-dependent (a) thermopower and (b) electrical conductivity of SLG and FLG films on glass substrates.

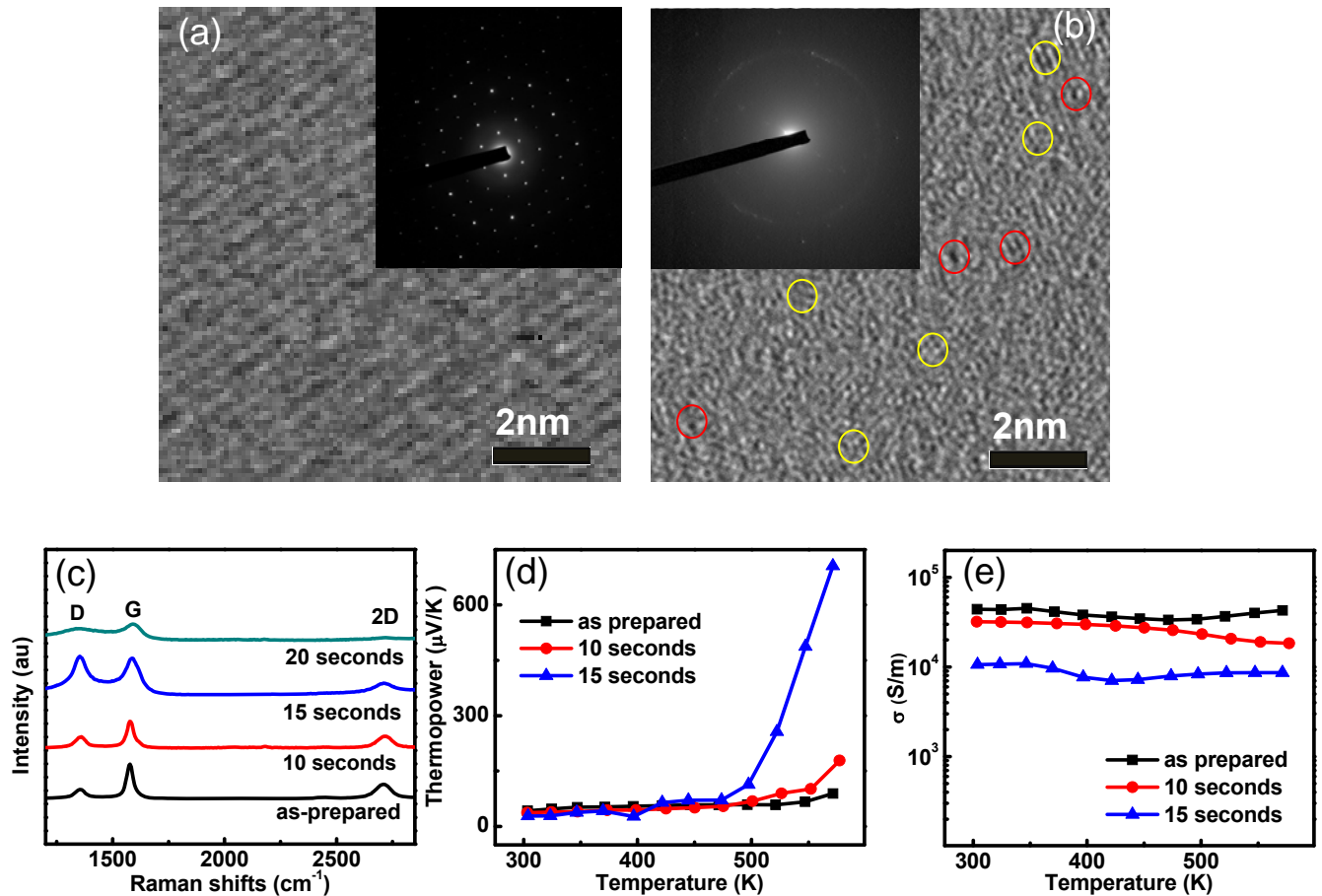


Figure 3. Atomic structure changes and thermoelectric properties before and after oxygen plasma treatment. **(a-b)** HRTEM images of FLG films **(a)** before and **(b)** after oxygen plasma treatment, illustrate the some atomic structures becomes disordered after oxygen plasma treatment. The yellow circles highlight small crystals of carbon in such film while the red circles point out the disordered arrangement of carbon atoms. The insets in **(a-b)** shows the corresponding SAED pattern, which confirms the crystalline nature of the pristine FLG film and amorphous for samples after oxygen plasma treatment. **(c)** Raman spectra of the FLG film after 10, 15, and 20 seconds oxygen plasma treatment. **(d-e)** Temperature-dependent **(d)** thermopower and **(e)** electrical conductivity for the FLG films after different oxygen plasma treatments.

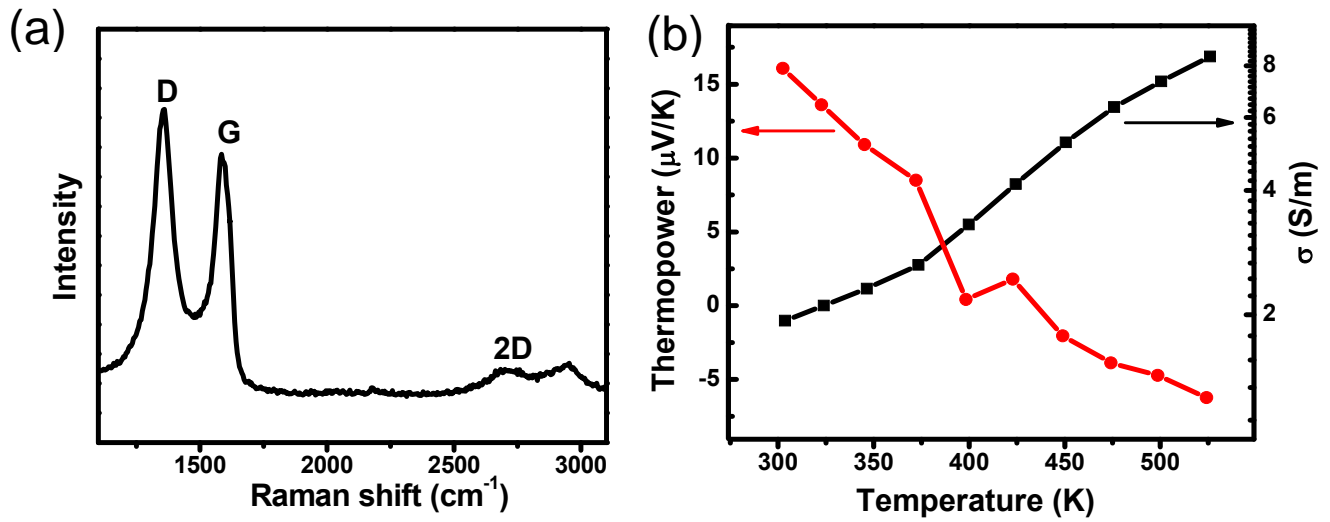


Figure 4. Characteristic and thermoelectrical properties of rGO. (a) Raman spectra of the rGO film. (b) Temperature-dependent thermopower and electrical conductivity of the rGO film.