



# Tuning the plasmon resonance and work function of laser-scribed chemically doped graphene



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## ABSTRACT

Here, we present terahertz spectroscopy study on laser scribed graphene (LSG) doped with monovalent Na<sup>+</sup> cations (LSG/MNCs), silver nanoparticles (LSG/SNPs), and silver nanowires (LSG/SNWs), in the frequency range from 0.06 to 3 THz. The terahertz absorption peaks observed at  $\approx 1.98, 2.06, 2.73,$  and  $3.06$  THz are attributed to the collective oscillations of free carriers in LSG, LSG/MNCs, LSG/SNPs, and LSG/SNWs, respectively. The plasmon peak position and Fermi energy  $E_f$  of LSG doped samples are shifted to higher energy compared to undoped LSG indicating the n-doping of graphene. The  $\sigma_{dc}$  and the charges concentration  $n$  show higher values in case of LSG/SNWs compared to other doped samples. This is mainly because silver nanowires create conducting paths between the neighboring graphene sheets. The charge density  $n$  of the LSG and LSG doped samples versus  $E_f$ , scales as  $n^{1/4}$ , illustrates power-law behavior which is the signature of the two-dimensional massless Dirac electrons.

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## 1. Introduction

Since the discovery of graphene by K. Novoselov and A.K. Geim [1], graphene agitates the scientists' curiosity to explore its unusual properties, especially optical and electronic properties. This fact can be seen as a sequence of the unique graphene's crystal structure. Graphene is two dimensional (2D) honeycomb lattice and consists of two carbon sublattices. The quantum mechanical hopping between the two carbon sublattices leads to the formation of two cosine-like energy bands. The intersection of the two bands near the edges of the Brillouin zone yields the conical energy spectrum. Accordingly, the quasiparticles in graphene exhibit a linear dispersion, within  $\pm 1$  eV of the Fermi energy, as if they were massless relativistic particles [2–4].

Many approaches have been used to produce graphene such as

the reduction of graphene oxide (rGO) [5,6], epitaxial growth [7], and chemical vapour deposition (CVD) [8]. However, the optical and electronic properties of graphene prepared by the above mentioned methods are far from the incredible properties of the graphene produced by the exfoliation method [1,9]. Chemically prepared graphene oxide (GO) can be produced by cost-effective chemical methods with a high yield. In addition, it possess high hydrophilicity, which enables the formation of highly stable aqueous colloids. The stable hydrophilic GO aqueous solutions facilitate the precise doping of GO with different metals and alkali metals and formation of GO thin films over many types of substrates as well. Therefore, the reduction of GO is definitely a key approach to increase the performance of graphene-based devices. Different methods have been used to reduce graphene oxide including, thermal [10], chemical [11], microwave [12], photocatalytic [13], electrochemical [14], and laser scribe [15]. Among those methods, the laser scribe reduction can produce rGO films with a much higher conductivity. In addition, rGO patterns can be drawn directly by commercial pre-programmed computer DVD drive or commercial CO<sub>2</sub> laser cutter to produce more complicated and delicate graphene circuits [11].

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Tuning the electronic band structure of graphene in a controlled manner is a crucial step towards the implementation of graphene into devices. Recently [16–21], organic molecules, alkali metals, and gas-phase doping of the CVD grown graphene were used to modulate the carriers concentrations as well as the carriers type. The addition of donor or acceptor atoms to graphene has been proposed as a means of controllably shift the electronic bands of graphene [22]. Shi et al. [23] showed that CVD grown graphene is hole doped when immersed in AuCl<sub>3</sub> solution and its work function up-shifted by 0.5 eV. Furthermore, Song et al. [24] reported that the work function of graphene is modified when graphene is contacted with metal. It is either pinned to a particular value (about 4.62 eV) regardless of the work function of the metal as in the case of Pd or Au or pinned to the work function of the metal when graphene doped with Cr/Au or Ni [24].

Researchers have given great efforts to study the field of plasmonics in 2D materials, particularly after the recent observations of the terahertz plasmon peak in 2D graphene. The plasmonics resonance observed in 2D materials are significantly provide great opportunities to construct new optical devices for variety of plasmonic and THz applications, such as detectors, polarizers, and antennas [25,26]. Earlier investigations on the nature of tuning the plasmonic resonance of graphene have been probed using terahertz [27,28], and infrared spectroscopy [29–31]. The experimental studies have been focused on tuning the plasmonic resonance by changing the dimensions of the graphene sheets, so called graphene nanoribbons, varying the graphene carriers density by applying electric field or by chemical doping [27,32]. Garcia et al. [32] showed that such plasmon frequencies can be tuned by controlling the nanoribbon width ( $w$ ), where plasmon excitation scales as  $w^{-1/2}$ . In addition, graphene plasmonic resonances have been tuned by direct adsorption of graphene on electrons rich metal substrates such as silver, aluminum, and copper [18,27,28,32–35] or with holes through adsorption on metal substrates with a work function higher than that of graphene, as in the case of gold and platinum [35]. For hybrid CVD graphene/silver nanowires and mechanically exfoliated graphene/metal nanostructure, the carriers concentration near the vicinity of silver nanowires was estimated to reach  $9 \times 10^{13} \text{ cm}^{-2}$  after applying more than 25 V [16,28]. Several terahertz spectroscopy studies showed different charge density values for single layer CVD grown graphene;  $4.6 \times 10^{12} \text{ cm}^{-2}$  for CVD graphene on Cu substrate [36],  $4 \times 10^{12} \text{ cm}^{-2}$  for CVD graphene on Si substrate [37], and  $2.25 \times 10^{13} \text{ cm}^{-2}$  for CVD graphene on insulating substrates without a gate [38].

In spite of the large number of extensive terahertz spectroscopy investigations [18,27,28,39,40], the doping-induced phenomena in the graphene are not yet fully covered, which affects the low-energy properties close to the Fermi level, work function modifications, and interaction between graphene and surrounding environment. To the best of our knowledge, no experiments so far have directly resolved the tuning of the plasmonic resonance in graphene microstructures by direct n-doping using electrons rich materials of different sizes and shapes.

Here, we report on the THz spectroscopy attenuated total reflection (ATR) measurements on laser scribed rGO. The work function of graphene was modified by doping chemically prepared GO with monovalent Na<sup>+</sup> cations (MNCs), silver nanoparticles (SNPs), and silver nanowires (SNWs). Several characterizations methods such as high resolution transmission electron microscope (HRTEM), scanning electron microscope (SEM), Raman spectroscopy, and THz spectroscopy have been used to give valuable information on the distribution, morphology, structure, and compatibility of the graphene hybrid structures. We investigate the effect of the significant increases of doped electrons on the Drude

weight  $D$ , charge density  $n$ , shift of plasmon peak, and Fermi energy  $E_F$ . The effect of doping of Na<sup>+</sup> ions, Ag nanoparticles, and Ag nanowires on the plasmonic properties of laser scribed rGO was compared to those of undoped graphene and previously published data.

## 2. Experimental section

### 2.1. Samples preparation

**Preparation of Graphene Oxide (GO):** In order to obtain fully oxidized graphene sheets with large lateral sizes, dry expandable graphite flakes (3772, 300  $\mu\text{m}$  nominal size, Asbury Carbons, USA) were first thermally treated at 1050 °C for 15 s. The resultant expanded graphite (EG) was used as the precursor for GO preparation. The modified method for the preparation of GO done by Marcano et al. [41] was used. Briefly, 3.0 g of EG was added to a 9:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (360:40 mL) in ice bath. Then, 18 g of KMnO<sub>4</sub> was added very slowly to the mixture. The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and then poured onto ice (400 ml deionized water with 3 ml 30% H<sub>2</sub>O<sub>2</sub>). The resultant GO paste was washed with 1:10 HCl solution (5 L). Then, the GO paste was washed several times by deionized water, until the pH is nearly 7. The GO powder was obtained by dehydration at 60 °C for 6 h under vacuum and then dispersed in water by ultrasonication. The obtained brown dispersion was subjected to 30 min centrifugation at 4000 rpm to remove any un-exfoliated GO sheets.

**Preparation of Graphene Oxide/Silver Nanowires (GO/SNWs):** Silver nanowires were prepared using typical polyol method [42]. In typical experiment, 0.4125 g of PVP was dissolved in 55 ml ethylene glycol, then the solution was heated for 1 h at 160 °C. Silver nitrate (AgNO<sub>3</sub>) (0.3 g) was dissolved in 2.5 ml ethylene glycol and 1.125 g potassium chloride was dissolved in 2.5 ml ethylene glycol. The two solutions were mixed together and then added to the hot PVP solution. The solution turned dark gray indicating the formation of silver nuclei. Then, 0.465 g of AgNO<sub>3</sub> in 40 ml ethylene glycol was injected to the silver nuclei solution with a rate of 1.3 ml/min. The reaction was continued for 30 min. A 60 mg of GO was dispersed in 20 ml EG using ultrasonication for 2 h. The GO solution was heated to 160 °C for 1 h, then 10 mg of hot EG silver nanowires solution was added to GO solution and thermally stabilized at 160 °C for 1 h. The solution was cooled down and the GO/SNWs was then precipitated with acetone and centrifuged at 1000 rpm for 10 min. The supernatant was washed many times with ethanol through centrifugation at 5000 rpm. Then, the solution was dispersed in 20 ml of deionized water.

**Preparation of Graphene Oxide/Silver Nanoparticles (GO/SNPs):** Silver nanoparticles were loaded over GO sheets using Murphy et al. method [43]. The preparation method is as follows: a 20 mL suspension of GO (3 mg/mL) was stirred thoroughly with 10 mg AgNO<sub>3</sub>. Aqueous sodium borohydride (NaBH<sub>4</sub>, 360  $\mu\text{L}$ , 250 mM) was added dropwise to the GO/AgNO<sub>3</sub> suspension under vigorous stirring. The suspension was stirred for additional 5 min and then stored in the dark for later use. Fig. 1 (a) illustrates the preparation scheme for synthesizing GO, GO/SNPs, and GO/SNWs.

**Doping of Graphene Oxide with monovalent Na<sup>+</sup> cations (GO/MNCs):** Doping of GO by monovalent Na<sup>+</sup> cations was performed according to Ref. [44]. Briefly, 60 mg GO was immersed in aqueous NaOH solution at pH 10 to a concentration of 3 mg/ml. Then, the exfoliation and dispersion were carried out by ultrasonication for 1 h. Subsequently, the aging process was performed for several hours. The ratio of the sodium cations to GO was found to be  $\approx 10\%$ . According to Ref. [44] the chemically reduced GO/MNCs revealed an excellent electrical conductivity of 97,500 S/m. Therefore, we

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