Carbon 123 (2017) 380–384

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Ultraviolet-light-induced electron transfer between chlorine anions and graphene

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ARTICLE INFO

Article history:
Received 26 May 2017
Received in revised form
21 July 2017
Accepted 24 July 2017
Available online 24 July 2017

ABSTRACT

Outer-shell electrons of singly-charged anions are allowed to be detached by absorbing photons with appropriate energy that is larger than the corresponding atomic electron affinity. In an anion-graphene system, these escaped electrons face the possibility of travelling to graphene through the electron-exchanged path that originates from the anion-graphene orbital overlapping. Using electrical measurements, we observe that the hole concentration of gold-chloride-functionalized graphene decreases upon ultraviolet-light impingements, yet by contrast it persists under visible lights. Then we identify the governing mechanism in which chlorine anions are neutralized to gaseous molecules, thus donating electrons to graphene, subsequently elevating the Fermi level, and lowering the electrical conductivity in graphene. This mechanism is validated by field-effect-transistor-based Dirac-point-shift measurements that reveal Fermi-level and carrier-mobility variations of graphene. Raman statistical analyses and X-ray photoelectron spectroscopy measurements are employed to further confirm this electron-transfer-related process. Our study can be applied to designs of anion-graphene-embedded devices for sensing as well as energy harvesting.

1. Introduction

Binding an extra electron, a ground-state neutral atom is reduced to a singly-charged anion, and simultaneously releases a certain amount of energy (the atomic electron affinity, *EA*) [1,2]. Naturally, regarding a reversed physical process as a quantum probability event, outer-shell electrons of these anions are allowed to be detached by absorbing photons with appropriate energy ($\hbar\omega > EA$). In anion-graphene systems, these excited electrons may be captured by graphene, in which carbon atoms with spatially conjugated p_z orbits are hexagonally arranged [3,4], leading to the Fermi-level elevation [5] and the charge-carrier-mobility variation of graphene. Therefore, tracking and analyzing electrical characteristics of graphene, we can monitor the photon-induced electron-transfer process between adsorbed anions and graphene.

In this study, monolayer graphene is spin coated with the gold chloride ($AuCl_3$), which has been widely used to modulate the Fermi level and the electrical conductivity of graphene-related materials [6–8] for the purpose of applying these sp^2-carbon-based substances to various electrical devices [9–11]. Seizing electrons in graphene, gold ions are reduced to atoms which subsequently aggregate into nanoparticles [12], such that graphene becomes positively charged and adsorbs chlorine anions by the strong Coulomb force. Generally, if such a chloride-anion-graphene system, which is stable in the ambient condition for days, is exposed to the visible light ($\hbar\omega$ < 3.18 eV,) the electrical conductivity is capable of remaining unchanged. We discover that, by contrast, this conductivity behaves differently when the system is exposed to the ultraviolet (UV) light. Then we identify a governing mechanism, in which chlorine anions bond together to form gaseous molecules accompanied by offering electrons to the underlying graphene. To validate this mechanism, we conduct Dirac-point-shift measurements as well as Raman statistical analyses that reveal variations of graphene's Fermi levels under the UV-light

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http://dx.doi.org/10.1016/j.carbon.2017.07.084
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exposure. Finally, by measuring electrical-signal changes of the functionalized graphene, we obtain a spatially-resolved digitalized map showing UV-light-intensity distributions.

2. Result and discussion

We transfer CVD-grown graphene [13,14] onto SiO_2 (300 nm)/Si substrates (Fig. 1a and b), and then coat it with the gold-chloride solution using nitromethane as the solvent (S1, S2, and Fig. S1 in Supplementary Information, *SI*). The interaction originating from the overlapping between graphene's $2p_z$ orbits and gold-ion 6s orbits [15] allows electrons in graphene to transfer to gold ions to equilibrate energy differences [16]. After seizing electrons from graphene, these gold ions neutralize into atoms, and then aggregate to become nanoparticles [17] (Fig. 1c). Due to the occurrence of this electron transfer, the Fermi level lowers [18] and graphene becomes positively charged (p-type doping), leading to binary Raman-peak blue shifts [19] (Fig. S2 in *SI*).

Unexpectedly, upon the irradiation of the UV light, the electrical resistance experiences the tendency to restore to its originally undoped value. By contrast, it does not respond to the impingement of visible lights (Fig. S3 in *SI*). Here, we identify a photon-induced electron-transfer-related mechanism that governs this tendency (Fig. 2). In this mechanism, positively-charged graphene sheets adsorb chlorine anions by the strong Coulomb force, such that these anions can barely move on the graphene's surface under thermal perturbations ($k_BT \sim 25.9$ meV at 300 K). The strength of this electrostatic attraction is stronger than that of van der Waals force (physisorption), whereas weaker than the counterpart of the covalent bonding (chemisorption). However, absorbing UV photons ($E_{UV} \sim 4.16$ eV), chlorine anions neutralize into atoms by emitting outer-shell electrons and are capable of migrating. The *EA* (~ 3.613 eV) of chlorine atoms [20] is approximately equivalent to a threshold, which denotes the lowest photon energy required to detach an electron from a chlorine anion [21]. The atomic migration allows anions to develop into neutralized gaseous chlorine that escapes from graphene substrates. Additionally, electrons emitted from anions are donated to graphene, and then they descend rapidly to unoccupied lower-energy levels in the π band without radiation [22]. This electron injection reduces the hole concentration in this p-type chlorine-anion-adsorbed graphene, leading to the electrical conductivity decreases.

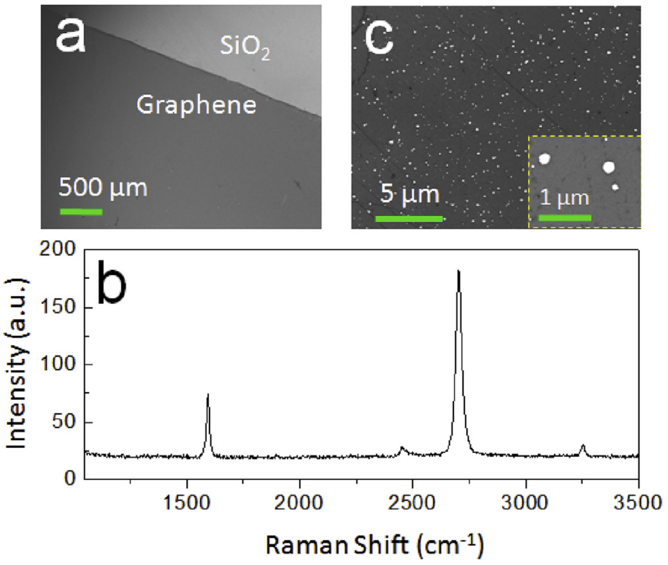

Fig. 1. (a) SEM image of transferred monolayer graphene. (b) Raman single spectrum of the graphene/SiO_2 sample. (c) SEM image of transferred graphene after being doped with gold-chloride solution at the concentration of 1 mg/ml. Inset in (c) shows gold nanoparticles with $50 \sim 200$ nm diameter. (A colour version of this figure can be viewed online.)

To validate this claimed mechanism, we conduct analyses on Dirac-curve characteristics [5,23] of gold-chloride graphene (GCG) embedded in field effect transistors (FETs) (Fig. 3a). Prior to spin-coating with the dopant solution, the gold-chloride-absent graphene (PG) is slightly p-doped as the adsorption of oxygen molecules and moistures [24–26] ($V_{Dirac} = 15$ V, the black curve in Fig. 3b). In the vacuum condition (10^{-6} *Torr*), the p-type graphene becomes neutralized because of the desorption of these electrophilic molecules (Fig. S4 in *SI*). As we conduct the coating, this p-doped effect is further enhanced, with the evidence that the V_{Dirac} shifts eastward (the red curve), demonstrating that the electron transfer between graphene and dopants leads to the drop of Fermi levels and the increase of hole concentrations in graphene. Under UV-light impingements, the V_{Dirac} gradually reverts the shift westward, and eventually ceases to shift as the exposure time elapses (Fig. 3b). Owing to the combination of the systematic electrical neutrality and the gold-ion-induced hole-doping effect, the eventually-stationary Fermi level is situated lower than the counterpart of PG. By contrast, V_{Dirac} of PG persists under the irradiation of UV lights in the ambient condition (Fig. S5 in *SI*). In terms of electrical-conductivity variations, neither hydrogen ions nor hydroxyl anions will alter the hole concentration for both PG and GCG that are exposed to UV lights (S3 in *SI*).

In thermal equilibrium under zero gate voltage, the major-carrier concentration (n) and the Fermi level (E_F) of graphene can be estimated by

$$n = C_i|V_{Dirac}| \cdot |q|^{-1} + n_0 \tag{1}$$

and

$$|E_F - E_{Dirac}| = \alpha\sqrt{|V_{Dirac}|}, \tag{2}$$

where $C_i = \varepsilon_0\varepsilon_r d^{-1} \sim 1.151 \times 10^{-4}$ F m^{-2}; $\alpha = \sqrt{\pi C_i|q|^{-1}}\hbar v_F \sim 31.3$ meV V$^{-0.5}$; $n_0 = (\pi/6)(k_BT/\hbar v_F)^2$ the intrinsic carrier concentration of graphene [27]; and $E_{Dirac} = 0$ for convenience (S4 in *SI*). Accordingly, with the absorption of UV-light photons, the V_{Dirac} shifts gradually from 57.8 ± 0.8 V (the extreme point of Lorentz-fitted red curve in Fig. 3b) to 28.0 V, indicating that the hole concentration of GCG decreases from 4.24×10^{12} to 2.09×10^{12} cm^{-2} as the Fermi level rises from −0.238 to −0.166 eV (Dirac cones in Fig. 3a; $n \sim 1.16 \times 10^{12}$ cm^{-2} and $E_F \sim -0.121$ eV for PG). This Fermi-level elevation can be attributed to the photon-induced electron-transfer-related process, in which electrons in chlorine anions transfer to the positively-charged graphene. Additionally, we calculate the carrier-mobility (μ) variation that reflects the change of the Coulomb-force-induced long-range scattering [28] according to

$$\mu = L(WC_iV_{sd})^{-1}(\partial I_{sd}/\partial V_g), \tag{3}$$

where L and W denote the conductive-channel length and width; V_{sd} the source-drain voltage [29]. Because of the scattering enhancement induced by numerous adsorbed charged impurities [30,31], carrier mobilities of GCG become much lower than counterparts of PG (5607.2 and 3991.4 cm^{2}V^{-1}s^{-1} for holes and electrons). However, both hole and electron mobilities increase gradually under UV-light impingements (3699.3 to 4820.7 cm^{2}V^{-1}s^{-1} for μ_h; 1216.3 to 1602.5 cm^{2}V^{-1}s^{-1} for μ_e,