Title
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Permalink
https://escholarship.org/uc/item/7z54x948

Journal
Nature communications, 9(1)

ISSN
2041-1723

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Publication Date
2018-05-23

DOI
10.1038/s41467-018-04385-4

Peer reviewed
Extremely stable graphene electrodes doped with macromolecular acid

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Although conventional p-type doping using small molecules on graphene decreases its sheet resistance ($R_{sh}$), it increases after exposure to ambient conditions, and this problem has been considered as the biggest impediment to practical application of graphene electrodes. Here, we report an extremely stable graphene electrode doped with macromolecular acid (perfluorinated polymeric sulfonic acid (PFSA)) as a p-type dopant. The PFSA doping on graphene provides not only ultra-high ambient stability for a very long time (> 64 days) but also high chemical/thermal stability, which have been unattainable by doping with conventional small-molecules. PFSA doping also greatly increases the surface potential (~0.8 eV) of graphene, and reduces its $R_{sh}$ by ~56%, which is very important for practical applications. High-efficiency phosphorescent organic light-emitting diodes are fabricated with the PFSA-doped graphene anode (~98.5 cd A⁻¹ without out-coupling structures). This work lays a solid platform for practical application of thermally-/chemically-/air-stable graphene electrodes in various optoelectronic devices.
Graphene has outstanding electrical, mechanical, and optical properties1–3, so it has been regarded as an alternative to indium tin oxide (ITO), which is the conventional transparent electrode in optoelectronic devices but is not suitable for electrodes in flexible optoelectronics due to its brittleness and increasing cost6,7. Since the development of chemical vapor deposition (CVD) methods to produce high-quality and large-area graphene2–5, much research has been devoted to applying graphene in flexible electronics such as organic light-emitting diodes (OLEDs)8–16, organic solar cells17–19, and organic transistors20–22. However, pristine graphene has high sheet resistance ($R_{\text{sh}} > 300 \Omega \text{sq}^{-1}$) and low work function (WF $\sim 4.4$ eV) which are still inferior to those of ITO ($R_{\text{sh}} = 10 \Omega \text{sq}^{-1}$, $R_{\text{sh}} = 4.8$ eV), so pristine graphene must be modified before it can be a practical replacement for ITO electrodes23,24.

Various researchers have used chemical doping to control the electrical properties of pristine graphene23–25,29–35. Dopants used in graphene for electrodes to date have been mainly classified into two types: (1) small molecules3,8,25, and (2) transition metal oxides14,36,37; both exploit charge transfer on the graphene surface. Charge-transfer doping of graphene with small-molecule dopants such as inorganic small-molecule acids (e.g., HNO$_3$, HCl, H$_2$SO$_4$)8,23 and metal chlorides (e.g., AuCl$_3$, FeCl$_3$)26–29 has been widely used and developed to increase the electrical conductivity of graphene; however, graphene that is doped with inorganic small-molecule acids has serious environmental instability, which has been considered as a great impediment to practical application of graphene electrodes. $R_{\text{sh}}$ of an HNO$_3$-doped graphene gradually increases under ambient conditions due to high volatility of small-molecule acids, and high temperature accelerates significant degradation in its electrical conductivity8. After doping with metal chlorides, reduction of metal cations can produce metal particles on the graphene surface; these have two deleterious effects: they can decrease the optical transmittance (OT) of the graphene, and if they are large, they protrude and provide leakage paths for electrical current in thin-film devices8,26–29. Also, transition metal oxides are not uniformly deposited on the graphene surface because the graphene lacks dangling bonds or surface functional groups. Therefore, thermal evaporation of transition metal oxide on graphene also roughens its surface38. Ideal chemical doping of graphene for practical use as an anode in electronic devices should achieve: (1) low $R_{\text{sh}}$, (2) high WF, (3) high stability against heat, chemical, and ambient conditions, (4) smooth film surface, and (5) high OT.

Here, we introduce a novel approach to macromolecular chemical doping that uses a polymeric acid, which has not been used for graphene doping and demonstrated extraordinary results on all kinds of aspects of stability (high temperature, chemicals, and air) and high WF; these characteristics are almost unattainable with conventional small-molecule acid doping. We use a perfluorinated polymeric sulfonic acid (PFSA) for application to flexible graphene anodes in optoelectronics. PFSA is composed of a perfluorinated carbon backbone and sulfonic acid groups. Due to the electron-withdrawing properties from electronic dipole of acidic proton in sulfonic acid groups, PFSA induces p-type doping of graphene. Furthermore, the perfluorinated carbon backbones have large ionization potential, which substantially increases the surface potential of graphene. Superior thermal and chemical stability of PFSA molecule provided outstanding stability of chemically doped graphene against high temperature heating and exposure to various chemicals including strong acids and bases39,40. Therefore, the PFSA is an ideal form of macro-molecular p-type dopant for graphene electrode. Our unconventional approach of using polymeric acid may stimulate research into high-stability graphene doping, and can be a starting point in the development of polymeric-acid dopants for ideal graphene electrodes.

Results

**Doping effects of a polymeric fluorinated acid on graphene.** We used non-volatile polymeric acid (i.e., PFSA) instead of volatile small-molecule acid (e.g., HNO$_3$) to dope graphene (Fig. 1a). To study PFSA doping characteristics on graphene, we spin-cast a PFSA on high-quality and large-area single-layered graphene (SLG) that had been prepared using CVD on Cu foil, followed by conventional wet-transfer4,8,10,14. PFSA doping on graphene did not degrade the optical properties of graphene: at wavelength $\lambda = 550$ nm, pristine four-layered graphene (4LG) had OT $= 90\%$, and PFSA-doped 4LG had OT $= 89\%$ (Fig. 1b).

Raman spectroscopy is a non-destructive tool to identify the doping characteristics, the number of layers, and the structural disorder in graphene41,42. Raman spectra were obtained from pristine and PFSA-doped SLG (Fig. 1c). The spectrum of the pristine graphene showed a very small D-band ($\sim 1350$ cm$^{-1}$), which indicates that high-quality graphene had been successfully grown and transferred onto the substrate with few defects. The spectrum of PFSA-doped graphene also showed a very weak D band; this result proves that solution-processed doping of the PFSA does not induce any significant structural defects in the graphene lattice. The G- and 2D-bands of the PFSA-doped graphene were up-shifted compared to those of pristine graphene (G-band shift: from 1587 to 1594 cm$^{-1}$, 2D band shift: from 2684 to 2696 cm$^{-1}$); this change indicates that PFSA causes p-type doping of graphene43.

To prove the uniformity of PFSA-doping over a large area, we prepared large area 4LG ($\sim 3 \times 4$ cm) on glass substrate, then performed spatial mapping of $R_{\text{sh}}$ by using the EddyCus $^\text{TM}$ TF map 2525SR system (Fig. 1d, e). Pristine 4LG without vacuum annealing showed $R_{\text{sh}} = 352.7 \pm 48.0$ Ohm$^{-1}$sq$^{-1}$. PFSA doping uniformly reduces the $R_{\text{sh}}$ of graphene throughout the large area, and PFSA-doping followed by 300 $^\circ$C annealing showed significant reduction in the magnitude and variation in $R_{\text{sh}}$ (Pristine: 352.7 $\pm$ 48.0 Ohm$^{-1}$sq$^{-1}$, PFSA-doped: 91.4 $\pm$ 30.1 Ohm$^{-1}$sq$^{-1}$) (Fig. 1d, e). This result demonstrates the spatial large-area uniformity of PFSA-doped graphene.

The PFSA-doped graphene had a flatter and smoother surface (root mean square roughness ($R_{\text{rms}}$) $\sim 0.495$ nm) than that of pristine graphene ($R_{\text{rms}}$ $\sim 1.47$ nm) (Supplementary Fig. 1). Peak heights along the cross-section of the PFSA-doped graphene were $< 1$ nm because deposition of thin polymeric layer can flatten uneven regions of the pristine graphene, such as wrinkles and grain boundaries. This result indicates that PFSA doping can yield a uniform surface of flexible graphene electrode without large particles.

**Thermal stability and doping mechanism.** The thermal stability of PFSA-doped and HNO$_3$-doped graphene samples was investigated. HNO$_3$ caused a stronger doping effect than PFSA: compared to pristine graphene, the HNO$_3$-doping reduced the $R_{\text{sh}}$ by $\sim 69.7 \pm 1.2\%$, which is more substantial than the reduction by PFSA doping ($\sim 52.4 \pm 0.9\%$). To verify doping stability under high temperature, each p-type doped graphene (asD in Fig. 2a) was thermally annealed at 100 $^\circ$C $\leq$ annealing temperature ($T_{\text{a}}$) $\leq 300$ $^\circ$C in ambient conditions.

High-temperature annealing affected $R_{\text{sh}}$ (Supplementary Table 1). Compared to $R_{\text{sh}}$ of the as-doped graphene, $R_{\text{sh}}$ of PFSA-doped graphene on Si/SiO$_2$ substrate gradually decreased as $T_{\text{a}}$ increased (up to $\sim 22.4\%$ decrease of $R_{\text{sh}}$ (asD) at $T_{\text{a}} = 300^\circ$C), whereas $R_{\text{sh}}$ of HNO$_3$-doped graphene on Si/SiO$_2$ substrate...
increased as $T_a$ increased ($\sim$119.6% increase of $R_{sh}$ (asD) at $T_a = 300^\circ$C) (Fig. 2a); this trend is due to the high volatility of HNO₃. These results indicate that thermal stability is much better in PFSA-doped graphene than in HNO₃-doped graphene.

Large-area mapping (> 3 cm × 4 cm) of $R_{sh}$ in the PFSA-doped graphene was performed after annealing at various $T_a$. Over the whole region, $R_{sh}$ decreased as $T_a$ of PFSA increased (Supplementary Fig. 2a–d). Potential difference after annealing at various $T_a$ was also identified using Kelvin probe measurement (Fig. 2b). The PFSA-doped graphene had a uniform WF over a large area (> 1.5 mm × 1.5 mm). PFSA-coating and annealing at 100 °C yielded ~0.73 eV increase of surface potential; this change is consistent with the results of ultraviolet photoelectron spectroscopy (UPS) (Supplementary Fig. 3). Thermal annealing also gradually increased the surface potential of graphene to ~1.01 eV at $T_a = 300^\circ$C. The $R_{sh}$ decrease and WF increase after high-temperature annealing indicate that it increases p-type doping.

To determine the mechanism by which PFSA dopes graphene, we performed density-functional theory (DFT) calculation of PFSA-doped graphene. For ease of calculation, we used the simplest molecular form of PFSA. In the most energetically favorable configuration of PFSA-doped graphene (Fig. 2c, d and Supplementary Fig. 4), the acidic proton in the sulfonic acid group (−SO₃H) faces towards graphene. PFSA doping increases the WF of graphene by ~0.71 eV (Fig. 2c), which is consistent with results of Kelvin probe (~0.73 eV) and UPS (~0.8 eV). Acidity of protons in sulfonic acid (−SO₃H) causes the electronic dipole interaction with graphene, thereby reducing the electron density of graphene (Fig. 2d, green clouds). The substantial increase in WF can be attributed to the electronic dipole interaction of the acidic proton in sulfonic acid (−SO₃H) as well as an interface dipole formed by the electronegative perfluorinated backbone on the graphene; this dipole caused by fluorinated substituents can induce a similar vacuum-level shift in self-assembled monolayers on the electrode surface. The increased surface WF of the PFSA-doped graphene can effectively reduce the hole-injection energy barrier from the anode to overlying organic layers in OLEDs. Thermal annealing would cause rearrangement of PFSA at high $T_a$. Thermal annealing causes the perfluorinated backbone that has low surface energy to become dominant at the film surface, and sulfonic acid groups (−SO₃H) in PFSA rearrange towards the underlying graphene. Therefore, high-temperature annealing of PFSA-doped graphene increases the p-type doping effect in PFSA-doped graphene.

To quantify the p-type doping effect in PFSA-doped graphene, we calculated the charge concentration ($n$) by using in-depth Raman spectrum analysis and the Dirac point shift in field-effect transistors (FETs). The hole-doping effect can be differentiated from the strain effect. To monitor changes in $n$ and strain as a function of $T_a$ after PFSA doping, we obtained a hundred Raman spectra for each graphene sample by raster-scanning an area of 10 μm × 10 μm, then verified the variation of G-band and 2D-band position of each spectrum (Fig. 3a). G-band and 2D-band distributions of pristine graphene showed $n \sim 3 \times 10^{12}$ cm⁻², which increased to $\sim 8 \times 10^{12}$ cm⁻² after PFSA doping without significant strain generated in the graphene layer. Without PFSA doping, thermal annealing did not increase $n$ in pristine graphene. However, PFSA-doped graphene caused gradual and considerable increase in $n$ as $T_a$ increased; this result indicates that increase of $n$ in PFSA-doped graphene can be attributed to rearrangement of PFSA at high $T_a$. Notably, PFSA-doped graphene treated at $T_a = 300^\circ$C showed $n \sim 11 \times 10^{12}$ cm⁻², which is three times higher than $n$ in pristine graphene (Fig. 3b, c). PFSA-doped graphene showed slight increase in strain (Pristine graphene: 0.1% to −0.2%, PFSA-doped graphene at
and PFSA-doped graphene annealed at various T_a. The error bars represent the s.d. of multiple measurement results. c. Calculated electrostatic potential of the most stable configuration of PFSA-doped graphene (inset: difference in work function between pristine and PFSA-doped graphene). d. Configuration of PFSA-doped graphene (top) top view, and (bottom) side view. Spheres: blue = oxygen, silver = sulfur, cyan = hydrogen, orange = fluorine, yellow = carbon. The isosurface of the charge density distribution difference is also shown in the figure. Isosurface level is 0.005e Å⁻³.

These results also support that rearrangement of PFSA at high T_a influences the n of PFSA-doped graphene because the number of acidic protons in the proximity of graphene increases. All measurements showed that thermal annealing caused R_{sh} decrease, WF increase and n increase in PFSA-doped graphene as T_a increased; these results are direct evidence that increased T_a influences the doping effect of PFSA.

Chemical and air stability. To quantify the doping stability of PFSA under various conditions, we compared R_{sh} changes of PFSA-doped and HNO₃-doped graphene under exposure to chemicals, and ambient conditions. To demonstrate the chemical invulnerability of PFSA-doped graphene, polar protic (deionized water, isopropyl alcohol (IPA)), polar aprotic (dimethyl sulfoxide), and non-polar solvent (toluene) were spin-coated on p-doped graphene samples, which were then gently annealed to remove residual solvents. All treatments significantly increased the R_{sh} of HNO₃-doped graphene on Si/SiO₂ substrate, but had negligible effect on R_{sh} in the PFSA-doped graphene (Fig. 4a and Supplementary Table 2).

We also tested the chemical stability by dipping HNO₃-doped or PFSA-doped graphene into a solution of strong acid (hydrochloric acid, K_a > 1), weak acid (acetic acid, K_a ~ 1.8 × 10⁻⁵), weak base (ammonium hydroxide, K_b ~ 1.8 × 10⁻¹⁵), or strong base (sodium hydroxide, K_b > 1) for 15 s. R_{sh} of HNO₃-doped graphene greatly increased after acid and base treatments (Fig. 4b and Supplementary Table 3). Especially, R_{sh} of HNO₃-doped graphene after sodium hydroxide treatment was unmeasurable using the 4-point probe method; this result can be attributed to tearing of the surface of HNO₃-doped graphene by treatment with strong base chemicals (Supplementary Fig. 6a). In contrast, the surface of PFSA-doped graphene remained smooth even in strong base solution, so R_{sh} of this graphene increased much less than it did in HNO₃-doped graphene (Supplementary Fig. 6b). These results demonstrate that p-type doping using macromolecular acid is stable against almost every chemical environment.

To verify the long-term air-stability of PFSA, we monitored the R_{sh} change of PFSA-doped and HNO₃-doped graphene under ambient conditions (Fig. 4c). Although HNO₃ doping reduced the R_{sh} of graphene to ~38.3% of the R_{sh} of pristine graphene, R_{sh} increased over 4 days to ~74.1% of the R_{sh} of pristine graphene. On the contrary, the PFSA-doped graphene showed decreased R_{sh} to
-55.4% compared to the $R_h$ of pristine graphene; this reduction in $R_h$ was retained for 64 days without noticeable change under ambient conditions. Before the investigation of graphene’s doping stability, pristine graphene samples were vacuum-annealed at 500 °C to eliminate inevitable p-type doping effects of residual dopants (e.g., PMMA, etchant, oxygen, water molecules)\textsuperscript{1,51} which were introduced during transfer process. We measured contact angles by using deionized water and diiodomethane on pristine, HNO$_3$- and PFSA-doped 4LG to calculate surface energies of the graphene according to p-type doping (Fig. 4c and Supplementary Fig. 7); the Owens–Wendt model was used to calculate the surface energy\textsuperscript{52,53}. The water contact angle of pristine 4LG was 55.3°; it increased to 96.7° when PFSA was doped on it; this change indicates that PFSA doping increased the hydrophobicity of the graphene surface. The calculated surface energy of the PFSA-doped graphene was ~21.69 mJ m$^{-2}$ (Supplementary Fig. 7 and 8). The hydrophobic surface with low surface energy of the PFSA-doped graphene can more stably maintain the p-type doping effect in ambient conditions than can HNO$_3$-doped 4LG (surface energy: 41.20 mJ m$^{-2}$). Similarly, increased WF by PFSA doping was also stably maintained for 10 days under ambient conditions (Fig. 4d), whereas the WF of HNO$_3$-doped graphene decreased from 4.57 eV to 4.43 eV after exposure to ambient conditions for 8 days (Fig. 4e).

We also performed conductive atomic force microscopy (c-AFM) (Supplementary Fig. 9) to spatially resolve the electrical properties of graphene films according to doping methods. In-plane conductance of HNO$_3$-doped and PFSA-doped graphene were monitored after 5 days in ambient conditions by measuring current between p-doped graphene and Sb-doped Si tip. p-Type doping with HNO$_3$ or PFSA did not affect the surface topography of graphene. PFSA-doped graphene film showed uniform current in surface mapping, but the HNO$_3$-doped graphene surface showed significant heterogeneity of in-plane conductance (Supplementary Fig. 9b).

Calculated $n$ from Raman spectroscopy (Supplementary Fig. 10) and FET (Supplementary Fig. 11) results quantitatively prove that PFSA doping of graphene is stable under ambient conditions. The outstanding doping stability of PFSA on graphene can be attributed partly to the affluent fluorinated alkyls in PFSA, which substantially reduces the surface energy of the PFSA-doped graphene surface; it would repulse the molecules of applied solvents or ambient air, and maintain the doping effect\textsuperscript{54}. 

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**Fig. 3** n changes of PFSA-doped graphene induced by thermal annealing. **a** Variations in 2D- and G- bands of pristine, HNO$_3$-doped and PFSA-doped graphene. **b** Histogram of $n$, and **c** averaged $n$ of thermally annealed pristine and PFSA-doped graphene with various $T_a$ calculated from Raman spectroscopy results. The error bars represent the s.d. of multiple measurement results. **d** Current vs. voltage characteristics (inset: optical microscopy image of graphene-based FET; scale bar, 200 μm), and **e** $n$ of pristine, and PFSA-doped graphene annealed at various $T_a$ calculated from Dirac point shift. Each box chart includes minimum, lower quartile (lower horizontal line), median (middle horizontal line), mean (hollow square), upper quartile (upper horizontal line), maximum, and discrete data.
The simplest PFSA-graphene configuration has binding energy of 0.79 eV, which is much larger than that of HNO3-graphene (0.33 eV). The configurations between each dopant and graphene suggest that the acidic proton of HNO3 is more exposed to outer circumstances than is the acidic proton of PFSA (Supplementary Fig. 4). In contrast to the parallel HNO3-graphene configuration (Supplementary Fig. 4a, b), PFSA has non-planar molecular configuration (Supplementary Fig. 4d, e). The non-planar configuration and higher binding energy between PFSA and graphene improves doping stability over that of HNO3 does; this coincides well with our experimental observations. Furthermore, these charge density calculations used the simplest molecule of PFSA, so binding energy between the dopant and graphene could be underestimated. Indeed, DFT calculation indicates that an increase in the length of the PFSA molecule gradually increases binding energy between the molecule and graphene (Supplementary Fig. 12, Supplementary Table 4, Supplementary Note 7). Therefore, the actual doping stability of macromolecular PFSA-doped graphene could be much higher than the calculation suggests.

X-ray photoelectron spectroscopy of p-doped graphene shows an intense F1s peak (~690 nm), and S2p peak (~170 eV) (Supplementary Fig. 13a); these peaks confirm that the PFSA molecule remains on the graphene surface: The C1s spectrum of PFSA-doped graphene revealed C–C sp2 bonding (~284.7 eV), with four PFSA-related chemical bonds (i.e., C–O–C (~286.5 eV), C–S (~289.6 eV), −CF2 (~292.4 eV), −CF3 (~294.0 eV)) 23,55, which can be confirmed in the chemical structure of PFSA (Supplementary Fig. 13b, c).

Graphene doping using other macromolecules (PMMA and PEDOT:PSS) showed weak p-type doping effect and poor ambient stability, respectively (Supplementary Figs. 14 and 15); these results exhibit the uniqueness of the graphene doping using PFSA (Supplementary Note 9 and 10).

Considering all the experimental observations and further analyses of PFSA-doped graphene, we can conclude that PFSA meets all the requirements of an ideal p-type dopant to produce a graphene anode: (1) large $R_{sh}$ decrease, (2) substantial increase in surface WF, (3) high stability against high temperature, chemicals, and ambient conditions, (4) smooth and uniform...
voltage, and doped graphene (Supplementary Fig. 18a). The OLED with graphene anode due to the increased surface WF of PFSA-doped graphene (~4.3 eV), hole injection from the pristine graphene anode is seriously obstructed, so an OLED with the pristine 4LG showed very low current density. When the graphene was doped with PFSA, the hole current density in the HOD was dramatically increased by a factor of > 10^3 due to a ~0.8 eV increase in the surface WF and reduced R

Optoelectronics application. To demonstrate the improved hole-injection capability of the PFSA-doped graphene anode in organic optoelectronics, we fabricated hole-only devices (HODs) and green-emitting phosphorescent OLEDs that had anode made of pristine or PFSA-doped 4LG (Fig. 5a). Because of the large energy difference (> 1.0 eV) between the highest occupied molecular orbital energy level of the N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1’-biphenyl)-4,4'-diamine (NPB) (~5.4 eV) and WF of pristine graphene (~4.3 eV), hole injection from the pristine graphene anode is seriously obstructed, so an HOD with the pristine 4LG showed very low current density. When the graphene was doped with PFSA, the hole current density in the HOD was dramatically increased by a factor of > 10^3 due to a ~0.8 eV increase in the surface WF and reduced R

Discussion

We used a macromolecular fluorinated acid, PFSA, as a chemical p-type dopant to give extremely stable chemical p-type doping for graphene. The PFSA-doped graphene met the requirements for ideal p-type doping of graphene anode: (1) large R

Non-volatility, strong binding to graphene, and chemical and thermal stability of PFSA can explain the excellent environmental stability of PFSA-doped graphene. We also fabricated HODs and OLEDs to demonstrate the superior hole injection and electroluminescent characteristics of devices that used the PFSA-doped graphene as an anode. An HOD that used the PFSA-doped graphene showed dramatic improvement of hole current, and OLEDs that used PFSA-doped graphene exhibited increase of luminous efficiencies: this result demonstrates the possibility of practical anode application of the PFSA-doped graphene due to its improved electrical conductivity and surface WF, and confirms that our PFSA is a promising p-type chemical dopant to make more ideal flexible graphene electrodes with excellent environmental stability, high WF, and high stability against all kinds of circumstances (high temperatures, chemicals, and ambient conditions).
Methods
Fabrication and characterization of graphene anodes. SLG was synthesized on Cu foil by CVD. The foils were heated to 1060 °C with 15-sccm flow of H2 gas and annealed for 30 min. As a carbon source, 60 sccm of CH4 gas was flowed for 30 min, then the Cu foil was rapidly cooled to room temperature. After synthesis of graphene on Cu foil, PMMA was applied by spin-coating polymer solution (996k, purchased from Sigma Aldrich) as a supporting polymer layer for graphene transfer. O2-plasma treatment etching (RIE) was performed to remove the graphene that grew on the bottom of the Cu foil. The foil was immersed in a CE100 (YMS tech) etchant solution for 1 h to etch the Cu foil, then rinsed with deionized water for several hours to remove the etchant residue. Flat-on-Cu SLG was transferred onto the target substrate. Before measuring the stability, we performed vacuum annealing on transferred graphene at ~500 °C. Glass substrates were used to investigate the OT, large-area uniformity, and ambient stability. To perform c-AFM, we used native Si as substrates. In other characterizations of PFSA doping effect (e.g., Raman spectroscopy, chemical-/thermal- stability test), we used Si/SiO2 (~300 nm) substrate. The supporting polymer layer was removed by soaking in an acetone bath. 4LG was stacked by repeating this process. Then 0.1 wt% tetrafluoroethyleneperoxyfluorine-3,6-dioxo-4-methyl-7-oxlenesulfonic acid copolymer (CAS number: 31175-20-9, Sigma-Aldrich) in IPA was spin-cast to chemically dope the graphene, then the sample was annealed at 100 °C for 10 min to remove the solvent. Raman spectra were obtained using a home-built setup operated with a 514-nm argon laser. PFSA-doped graphene is the total energy of PFSA-doped graphene, \( E_{\text{PFSA}} \) is the total energy of isolated PFSA molecule, and \( E_{\text{graphene}} \) is the total energy of the pristine graphene layer.

Data availability. The datasets generated during the current study are available from the corresponding authors upon reasonable request.

Received: 4 September 2017 Accepted: 19 April 2018
Published online: 23 May 2018

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