Nano Research 2015, 8(11): 3496–3504
DOI 10.1007/s12274-015-0849-0
Research Article

ISSN 1998-0124
CN 11-5974/O4

Direct low-temperature synthesis of graphene on various glasses by plasma-enhanced chemical vapor deposition for versatile, cost-effective electrodes

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Received: 18 May 2015
Revised: 19 June 2015
Accepted: 29 June 2015

KEYWORDS

graphene,
direct,
plasma-enhanced chemical vapor deposition (PECVD),
glass,
various,
low-cost

ABSTRACT

Catalyst-free and scalable synthesis of graphene on various glass substrates at low temperatures is of paramount significance to numerous applications such as low-cost transparent electronics and state-of-the-art displays. However, systematic study within this promising research field has remained scarce thus far. Herein, we report the direct growth of graphene on various glasses using a low-temperature plasma-enhanced chemical vapor deposition method. Such a facile and scalable approach guarantees the growth of uniform, transfer-free graphene films on various glass substrates at a growth temperature range of 400–600 °C. The morphological, surface wetting, optical, and electrical properties of the obtained graphene can be tailored by controlling the growth parameters. Our uniform and high-quality graphene films directly integrated with low-cost, commonly used glasses show great potential in the fabrication of multi-functional electrodes for versatile applications in solar cells, transparent electronics, and smart windows.

Graphene is deemed a miracle material with promising prospects in both fundamental research and practical applications [1–3], owing to excellent properties such as good mechanical strength and flexibility, and exceptionally high electrical and thermal conductivities. To fully realize the great potential of graphene, extensive efforts have been devoted to its rational production in a controllable and scalable fashion. In particular,

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large-area uniform graphene films have been fabricated by chemical vapor deposition (CVD) on metal surfaces at elevated temperatures [4–8]. However, such a route requires costly metal substrates, and additional transfer or catalyst removal procedures could hinder the graphene device performances and applications. Hence, it is of great significance to develop metal-catalyst-free CVD methods that allow direct synthesis of graphene on target dielectric substrates, enabling effective integration of graphene into various applications such as field effect transistors, transparent conductive electronics, gas detectors, and biosensors [9–15].

Recent years have witnessed many advances in direct synthesis of graphene by thermal CVD on a plethora of insulating substrates [11, 12, 16–20]. Growth at elevated temperatures (1,100–1,600 °C) gives rise to relatively high-quality graphene films. However, such a process is cost-ineffective because of large energy consumption and could also hinder the application of graphene in optoelectronic devices owing to potential thermal degradation; moreover, it imposes further limitations on the choice of substrates, e.g., commercial float glass substrates with relatively low softening points (ca. 620 °C). Hence, the game-changing breakthrough would be the development of reliable and scalable routes to produce uniform and high-quality graphene directly on insulating substrates at low temperatures.

One promising way to realize the aforementioned goal is employing plasma-enhanced CVD (PECVD) [21]. Compared to thermal CVD, a PECVD approach enables graphene deposition at a lower temperature with better control of film uniformity owing to the presence of energetic and reactive species generated in the plasma region. One pioneering study by Zhang et al. [15] on catalyst-free growth of nano-graphene films on various substrates dealt with the employment of PECVD at a substrate temperature of ~550 °C. Recently, Wei et al. [13] have demonstrated growth of high-quality graphene on sapphire and SiO_2/Si using a seeded PECVD method at quite low growth temperatures of 400–600 °C. Moreover, the potential for application of PECVD-grown graphene in transparent electronics and flexible strain sensors has also been explored [15, 22–24]. Thus far, despite the fact that extensive research has been conducted on low-temperature deposition of graphene on insulators, no systematic study has centered on the direct growth of graphene on various glass substrates, which, however, is highly desirable and versatile for cost-effective electronic and optoelectronic applications.

Here, we report the direct growth of graphene on various glasses through low-temperature PECVD using pure CH_4 as the precursor. Without the aid of any metallic catalyst, uniform, transfer-free vertically oriented graphene flakes can be directly formed on various glass substrates at a temperature range of 400–600 °C. The morphological, surface wetting, optical, and electrical properties of the obtained graphene can be modified by altering the substrate type, growth temperature, reaction time, and precursor concentration. The as-grown samples were tested as counter electrodes in dye-sensitized solar cells (DSSCs) and transparent conducting electrodes even in flexible electronics. Our approach, in principle, allows direct integration of graphene films with low-cost, universally used glass in a controllable and scalable manner. To the best of our knowledge, this work represents the first detailed investigation on the direct growth of graphene on various glasses at a low temperature.

Figure 1(a) depicts the schematic diagram of the PECVD apparatus employed in this work. Specifically, a homemade remote radiofrequency (13.56 MHz) system (100 W) was used. A quartz tube with an inner diameter of one inch was fixed to a single-zone electrical furnace. A photograph of the experimental set-up during a typical experiment is displayed in Fig. 1(b). Figure 1(c) illustrates our ability to directly synthesize graphene on various glass substrates by PECVD. As depicted in the photograph (see the figure caption for sample orders), we have succeeded in growing the graphene films on diverse types of glass including cobalt blue glass, tinted glass, quartz glass, blue float glass, fluorine-doped tin-oxide-coated (FTO) glass, borosilicate glass, sapphire glass, and brown float glass. The direct growth of graphene on such glasses was carried out by using a CH_4-PECVD process at a temperature range of 400–600 °C without the aid of any metallic species or catalysts. The growth methodology is described in detail in the Electronic Supplementary Material (ESM).

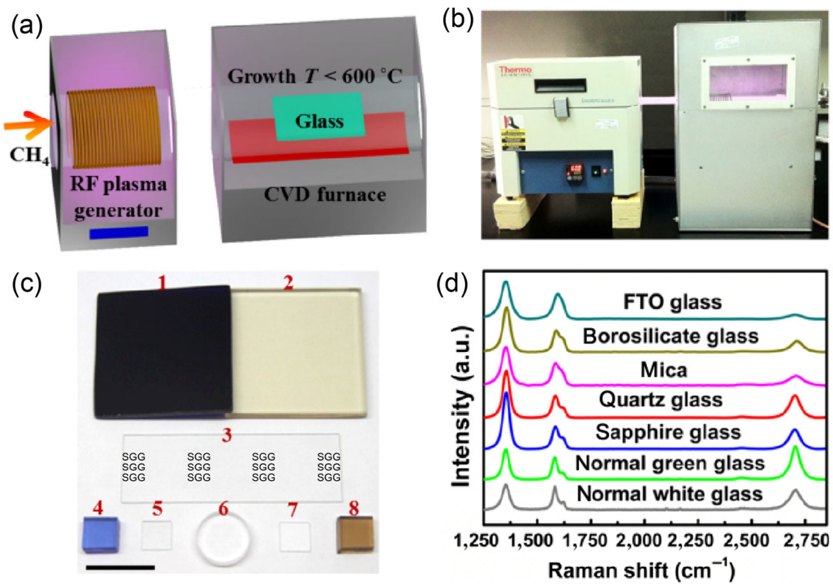

Figure 1 (a) Schematic illustration of the remote radiofrequency (RF) PECVD system. (b) Optical image of a real PECVD set-up, consisting of a lab-built RF plasma source (right) and a single-zone electrical furnace (left). (c) Photograph showing a collection of various types of glass used, indicating that the growth of graphene can be realized on a variety of glass substrates: 1. cobalt blue glass; 2. tinted glass; 3. quartz glass; 4. blue float glass; 5. FTO glass; 6. borosilicate glass; 7. sapphire glass; 8. brown float glass. Scale bar: 2 cm. (d) Raman spectra of graphene grown directly on different glass substrates by PECVD under identical conditions.

One of the advantages of our direct PECVD process is that graphene films can be formed on various glass substrates. To verify the possibility of its generalization, we carried out the graphene synthesis on various types of glass under identical PECVD growth conditions (5.6 standard cubic centimeters per minute (sccm) CH$_4$, 100 W, 600 °C, 1 h). Figure 1(d) displays Raman spectra of graphene grown on different types of glass, all of which show characteristic Raman peaks for graphene at 1,349 cm^{-1} (D band), 1,591 cm^{-1} (G band), and 2,690 cm^{-1} (2D band). All spectra were normalized to the G peak intensity for comparison. Technically, the synthetic feasibility of graphene films does not rely strongly on the growth substrates, but it is noted that the growth features (e.g., layer number, growth speed, film coverage) on different glasses vary slightly. For instance, the graphene grown on green float glass showed a high 2D peak, whereas the film obtained on FTO glass showed a small and broad one. This might be attributed to the distinct adsorption/diffusion capacities of hydrocarbon radicals on different substrates in plasma.

Notably, our approach centers on the direct synthesis of graphene films on commercial float glasses, which is particularly meaningful for practical applications owing to their widespread availability and low cost. Figure 2(a) shows a photograph of the bare white float glass (leftmost) and graphene-coated white glasses prepared with growth durations of 1 and 2 h, respectively (other growth parameters were identical: 10 sccm CH$_4$, 100 W, 550 °C). It is evident that the transparency of the sample decreases with prolonged growth time, indicating that the thickness of as-grown graphene films on glass can be well tailored by varying key growth parameters (the case of green glass is shown in Fig. S1 in the ESM). As shown in Figs. 2(b) and 2(c), different-shaped, commercial colored glass can also be successfully coated by graphene with excellent uniformity by means of PECVD, displaying a good transparency. Figure 2(d) shows a typical scanning electron microscopy (SEM) micrograph of graphene grown directly on white glass. Surprisingly, PECVD growth for 1 h results in a continuous network consisting of vertically oriented graphene flakes. Our observation is in accordance with that reported by Yang et al. [25], who employed a high-temperature (900 °C) PECVD route. The density of the flake can be tuned by adjusting the growth time (Fig. S2 in the

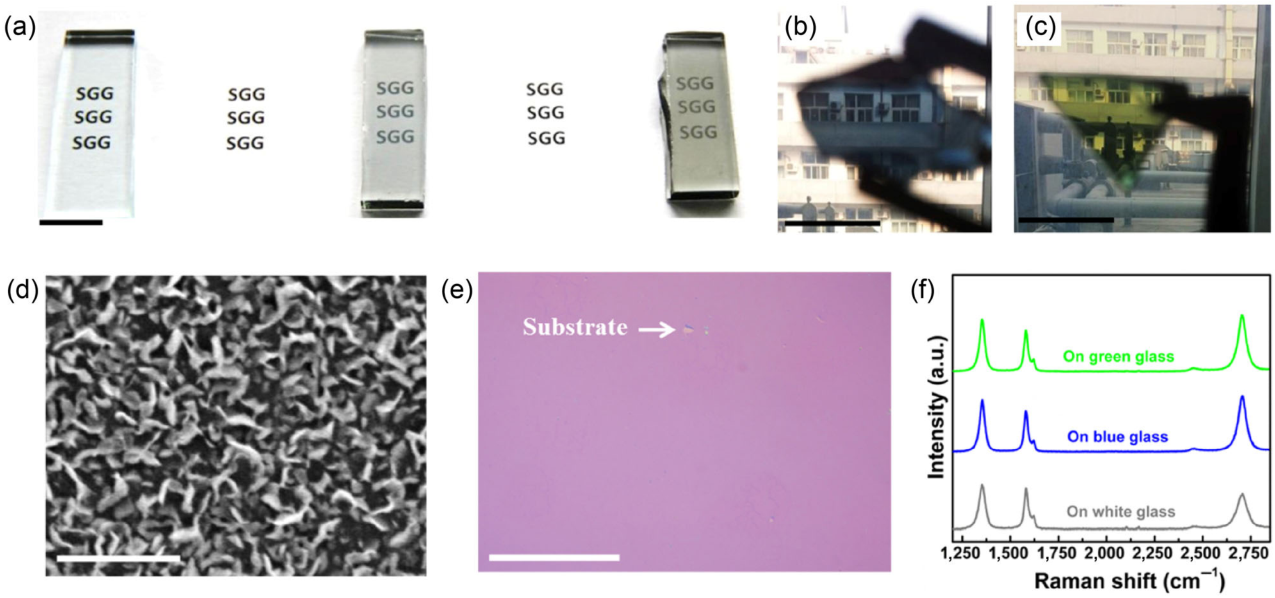

Figure 2 (a) Photograph of the white float glass substrates before (leftmost) and after PECVD graphene growth at 550 °C with different growth periods of 1 and 2 h. The photo was taken on printed letters of super graphene glass (SGG) as a background to illustrate the sample transmittance. Scale bar: 1 cm. (b) and (c) Photographs of PECVD graphene/blue (b) and green (c) float glass samples displaying good transparency. Scale bars: 2 cm. (d) SEM image of vertically oriented graphene films grown directly on white float glass by PECVD. Scale bar: 2 μm. (e) OM image of the graphene films transferred onto the SiO_2/Si substrate. Scale bar: 50 μm. (f) Representative Raman spectra of graphene grown directly on white and colored glass substrates by PECVD.

ESM). The obtained film was transferred onto a SiO_2/Si substrate for optical microscopy (OM) inspection. The uniform color contrast (Fig. 2(e)) implied excellent uniformity of the graphene films at a macroscopic level. The quality of as-grown graphene on different colored glass substrates undergoing identical PECVD procedures (6 sccm CH_4, 100 W, 600 °C, 1 h) was evaluated by Raman spectroscopy. The representative Raman spectra displayed in Fig. 2(f) clearly reveal the formation of graphene. The presence of the prominent D peak (~1,350 cm^{-1}) and the noticeable D′ peak (~1,620 cm^{-1}) indicates that our graphene films consist of quite a few small-sized graphene flakes with numerous open edges and intrinsic defects within the domains [26].

The typical procedure for the PECVD growth of graphene directly on glass substrates is illustrated in Fig. 3(a). It is well known that the energetic plasma can dissociate CH_4 into various active species, such as CH_x, C_2H_y, and atomic C and H [15, 27]. Such radicals are able to adsorb and collide onto the substrate surface, and play a dominant role in the graphene nucleation and growth. The observation of the formation of vertically oriented graphene flakes is interesting, and has also been reported in the catalyst-free growth of graphene by PECVD on insulating substrates such as SiO_2 [22, 28] and quartz [29]. It has been speculated that the electric field aligned perpendicular to the substrate surfaces offered by the plasma is responsible for the flake aggregation in the vertical direction [21, 25]. These textured graphene layers not only benefit electron transportation, but also possess high specific surface areas, making them ideal platforms for catalysis (e.g., counter electrodes in DSSCs) [30]. Raman spectra of the as-prepared graphene walls on white float glass substrates with different CH_4 concentrations (100 W, 600 °C, 1–2 h) are shown in Fig. 3(b). All spectra were normalized to the G peak intensity for comparison. It can be seen that the graphene quality is sensitive to the CH_4 flow rates. A sparse precursor concentration gives rise to almost no graphene formation, despite the prolonged growth duration. Higher concentrations of CH_4 would otherwise induce the graphene growth with possibly thicker layers. The sheet resistances of obtained graphene films can be adjusted accordingly, within a range of 0.85–1.55 kΩ·sq^{-1}, as

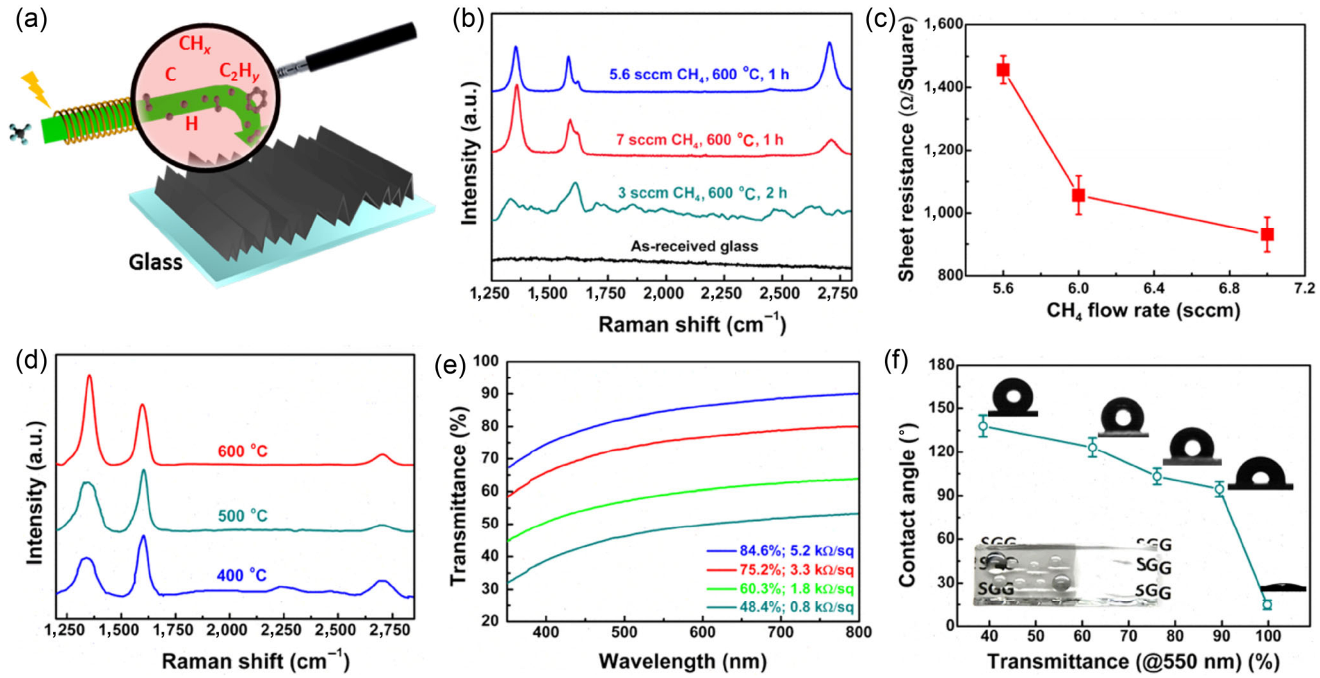

Figure 3 (a) Schematic of graphene growth on glass substrates by a direct PECVD route. (b) Raman spectroscopy characterizations of graphene grown directly on white float glass by PECVD with varied growth parameters. All Raman spectra were normalized to the G peak intensity. (c) Sheet resistance versus precursor concentration during synthesis of as-made graphene/white float glass samples. (d) Raman spectroscopy characterizations of graphene grown directly on FTO glass by PECVD at various growth temperatures. All Raman spectra were normalized to the G peak intensity. (e) Sheet resistance and UV-vis transmittance spectra in the wavelength range of 350–800 nm of the PECVD graphene grown directly on white float glass. (f) Sheet resistance versus optical transmittance for graphene/white float glass samples fabricated by direct PECVD. The inset shows the hydrophobic and hydrophilic natures of a patterned graphene/glass (left) and bare glass surface, respectively.

shown in Fig. 3(c). Figure 3(d) shows Raman spectra of the graphene films grown directly on FTO glass substrates at 400, 500, and 600 °C (other growth parameters were identical: 10 sccm CH$_4$, 80 W, 1 h). The graphene quality is apparently somewhat low. Growth at higher temperatures on FTO otherwise results in decreased graphene quality (higher Raman D peak intensity), which might be attributed to the fact that the FTO coating is continuously damaged in a low-pressure, elevated-temperature pumping environment, and it is difficult for graphene deposition to stay on such surfaces.

The catalyst-free PECVD growth of vertically oriented graphene flakes on glass substrates begins with the dissociation of a carbon feedstock, CH$_4$ in this case. Unlike in the thermal decomposition process at elevated temperatures in a thermal CVD, CH$_4$ can be readily dissociated to reactive carbon species in the plasma without a metal catalyst. This is followed by the adsorption/diffusion of such carbon fragments onto glass surfaces, which can be influenced by the distinct adsorption/diffusion capacities of hydrocarbon radicals on different glass substrates. Then, the high-density, active carbon fragments collide, further nucleate, and grow vertically upward owing to the crowding effects [21]. In particular, the existing electric field aligned perpendicular to the glass surface, which was induced by the plasma, contributes to the vertical growth of graphene flakes [25, 31].

Figure 3(e) shows the transparencies and sheet resistances for the graphene grown on white glass, demonstrating our ability to tune the optical and electrical properties of as-fabricated samples by tailoring the growth conditions. The transparency is reflected by the ultraviolet-visible (UV–vis) transmittance spectra, and the sheet resistance was measured by using the four-probe method without any pretreatment of samples (doping, annealing). In our experiment, a typical sample possessing a pristine sheet resistance of 3.7 kΩ·sq^{-1} with a transmittance of 79% can be reproducibly obtained. At a similar transparency, the electrical performance is comparable to that fabricated by direct PECVD on quartz and SiO_2 substrates [14, 15].

The direct coating of vertically oriented graphene films onto glasses would overwhelmingly alter the surface wetting behaviors of the pristine glass substrates. This can be reflected by the static contact angle (CA) measurements of pure water droplets. The optical transmittance versus the static CA value of the grown samples is plotted in Fig. 3(f). A pristine glass sample was used as a reference, displaying a complete wetting behavior with a CA of 10°–17°. The CA of the graphene samples with a transmittance (at 550 nm) of ~89% reaches ~95°. The CA value increases with decreasing transparency (corresponding to a prolonged growth time with a higher precursor supply during the PECVD synthesis); the largest obtained CA value was 143°. For a vivid demonstration, we performed water dropping tests on a patterned sample 1 cm × 3 cm in size (Fig. 3(f) inset); one can clearly observe that film-wise water aggregations are formed on a bare glass surface (right-hand side), whereas small water droplets stand up on the surface of graphene-coated glass (left-hand side), indicative of a distinct surface wetting behavior after PECVD graphene coating. In this regard, the morphological effect (textured surface) in combination with the surface chemistry of the graphitic flakes renders the thus-fabricated graphene/glass sample highly hydrophobic. Such a property would probably facilitate its application in multi-functional, low-cost, eco-friendly, self-cleaning windows and displays.

To demonstrate the potential for application in cost-effective solar cells, the directly grown graphene/glass samples were assembled as counter electrodes in DSSC prototype devices. Our fabricated DSSC encompasses a dye-sensitized nanocrystalline TiO_2 working electrode, an electrolyte solution containing a dissolved I^-/I_3^- redox couple, and a counter electrode made from our graphene/white float glass sample (Fig. 4(a)). Our direct PECVD graphene with thick layers displayed higher catalytic activities for the reduction of I_3^- ions than the transferred Cu-grown graphene (Fig. S3 in the ESM).

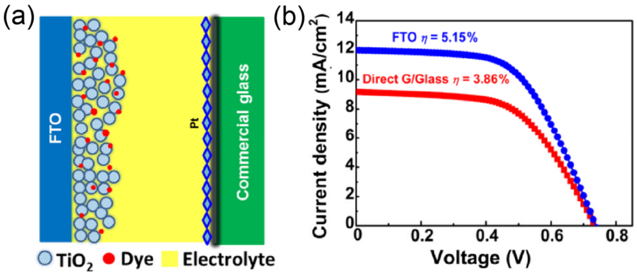

Figure 4 (a) Schematic diagram of the DSSC device based on a PECVD graphene/glass counter electrode. (b) *J*–*V* characteristics of the DSSC devices based on FTO/Pt and graphene/Pt counter electrodes.

The photocurrent density–voltage (*J*–*V*) plot of our graphene/glass-based DSSC devices is shown in Fig. 4(b). The overall power conversion efficiency (η) of our DSSC device reached 3.86% without any optimization process (V_{OC} = 0.735 V; J_{SC} = 9.2 mA/cm^2; FF = 57%, where J_{SC} is the short-circuit current, V_{OC} is the open circuit voltage, FF is the fill factor). This performance is comparable to that of our reference sample employing Pt/FTO as the counter electrode (5.15%), a widely used counter electrode in DSSCs. Our PECVD graphene/glass-based DSSC has efficiency comparable to those based on graphene nanosheet films on FTO (η = ~3.29%–6.81%) [30] and atmospheric pressure CVD (APCVD)-grown graphene (synthesized at 1,200 °C) on SiO_2 (η = ~2.95%–4.25%) [19], but superior to that assembled from reduced graphite oxide on FTO (η = ~0.2%–3.7%) [32] as counter electrode materials. Such results offer promising evidence that the directly grown PECVD graphene/glass samples could serve as low-cost electrode materials to replace cost-ineffective FTO in photovoltaic applications.

The directly grown graphene/glass sample was also tested in a range of transparent conductive applications that require uniform, cheap, flexible, yet high-quality graphene on transparent substrates. Figure 5(a) shows an optical image of a designed transparent circuit, which was fabricated based on PECVD graphene/ultra-slim Corning® Willow glass by virtue of photolithography. The OM image in the Fig. 5(a) inset presents the layout of an individual unit of the circuit. Our ongoing research involves exploring the exact functions of such circuits on glass, which might have potential for application in optoelectronics, gas/moisture/bio sensors, etc. For instance, the resistances

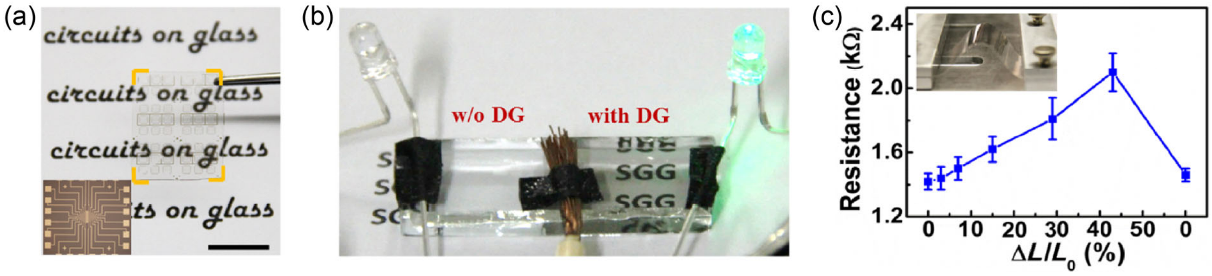

Figure 5 (a) Photograph showing an as-fabricated transparent circuit based on PECVD graphene/glass. The inset shows an OM image of an individual device layout of the circuit. Scale bar: 1 cm. (b) Photograph of a patterned PECVD graphene/commercial white float glass sample showing the transparent conductive property to light up a green LED indicator (right). The sample size is 1 cm × 3 cm. (c) Measured resistance versus bending variation for a graphene film grown directly on a 2 cm × 8 cm mica glass sheet. The inset shows the bending process.

of the patterned graphene within circuit devices would show a noticeable change due to the variations in the ambient environments, and such a resistance change can be selectively measured with the design of a specific circuit layout. Figure 5(b) displays a simple, patterned graphene-on-glass electrode that can light up a green light-emitting diode (LED) indicator, with a bare glass side serving as the reference.

Moreover, in view of the potential for integration into flexible electronic devices, the mechanical durability of directly grown graphene is an important factor. To the best of our knowledge, such a property has not been well studied thus far [27]. Here, we synthesized uniform graphene films on a flexible mica glass sheet (2 cm × 8 cm in size) and measured the resistance changes of the obtained samples by bending tests. Figure 5(c) shows the bending test results of the directly grown graphene electrode. The graphene film on mica can tolerate a bending variation ($\Delta L/L_0$) up to 45% and manages to fully recover after bending (Fig. 5(c) inset), indicating good mechanical properties. Such high bendability is attributed to the strong adhesion of the directly grown graphene to the flexible mica sheet.

In summary, we have demonstrated a simple, catalyst-free, low-temperature, and scalable PECVD route to synthesize uniform graphene films on various glass substrates. The morphological, surface wetting, optical, and electrical properties of the obtained graphene can be tuned by varying the growth parameters. Our approach offers the ultimate advantage of low-cost graphene growth on inexpensive glass and transfer-free device fabrication. The as-grown samples were tested as counter electrodes in DSSCs and transparent conducting electrodes even in flexible electronics. Our work centering on the direct growth of graphene on various glasses may represent a significant step towards large-scale, low-cost production of graphene glass for versatile applications at the industrial level.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (Nos. 2013CB932603, 2012CB933404, 2011CB921903, and 2013CB934600), the National Natural Science Foundation of China (Nos. 51432002, 51290272, 51121091, 51222201, and 11222434), the Ministry of Education (No. 20120001130010) and the Beijing Municipal Science and Technology Planning Project (No. Z151100003315013).

Electronic Supplementary Material: Supplementary material (experimental details, photographs of as-grown samples, SEM imaging and cyclic voltammetry measurements) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-015-0849-0.

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