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Substrate-Induced Graphene Chemistry for 2D Superlattices with Tunable Periodicities

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The advent of graphene, a 2D crystalline monolayer made of sp²-bonded carbon atoms arranged in a honeycomb lattice, has led to an explosion of interest in scientific and industrial communities because of its fascinating electrical, thermal, and mechanical properties.^[1,2] A unique feature of graphene is that all the carbon atoms in its basal plane are chemically accessible, providing a powerful pathway to tailor the physical and chemical properties of pristine graphene by using chemical approaches. Although graphene is generally chemically inert because of its giant delocalized π system, covalent functionalization has been demonstrated to be possible for the purposes of achieving bandgap engineering, doping-level modulation, chemo- and biosensing, new composite synthesis and largescale solution-processed production.[3-10] The covalent chemistry of graphene also provides a freedom to create new 2D materials and/or 2D graphene superlattices beyond graphene, creating a route to study the rich physics expected in attractive quantum systems.^[10–12] To date, several approaches have been reported for fabricating 2D graphene superlattices.^[13,14] However, most of these examples are based on the mask technique, which limits the structural resolution to only micrometer scales. An effective chemical approach to the nanometer scale graphene superlattices with tunable periodicities is highly desirable, which is crucial for generating a bandgap in the zero-gap pristine graphene for electronics and optoelectronics applications.^[14]

Because of its atomically thin feature, graphene is strongly influenced by substrate which can induce external influences, e.g., strain^[15,16] and charge puddles.^[17,18] Strain distorts the graphene's lattice and hence strongly influences its physical and chemical properties. Both experimental^[19,20] and theoretical^[21] studies have demonstrated that strain can build enormous

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pseudo-magnetic fields in graphene and engineer its electronic structure. Strain-induced superlattices can produce significant energy gaps in graphene and show a pseudo-magnetic quantum hall effect.^[21] Recently, it was also shown that straining graphene leads to a substantial increase of its reaction rate with diazonium salts and the final modification degree.^[22,23] Substrate-induced charge (hole or electron) puddles are found to increase the chemical reactivity of graphene toward diazonium functionalization.^[18] These phenomena strongly suggest the possibility of substrate engineering for controlling graphene's chemical reactivity on its basal plane for the purpose of fabricating 2D superlattices.

In this paper, we report a substrate engineering approach to periodically pattern the graphene basal plane for the purpose of fabricating 2D graphene superlattices (Figure 1a). This mask-free patterning technique is inspired by the old Chinese rubbing printing, in which the pigment is deposited over protrusions by rubbing hard rendering materials over paper while the depressions remain unpigmented. In our approach, the reactive species act as the pigment and the chemical reaction of graphene is guided by the underlying substrate with periodic protrusions. These predesigned protrusions introduce periodic compressive strain into the graphene basal plane by thermal annealing treatment because of graphene's negative thermal expansion coefficient.^[24,25] Moreover, the SiO₂ protrusions could induce charge puddles in graphene, which further increase the chemical reactivity of attached graphene.^[18] The existence of local strain and charge puddles could enhance the chemical reactivity of graphene, leading to a localized periodic functionalization on the graphene sheet. As a result, graphene superlattice can be achieved with the predesigned substrate. We have successfully fabricated various graphene superlattices with different periodicities in such a way. This substrate engineering technique allows for a well-controlled periodic modification of graphene, enabling the construction of various graphene-based electronic and optoelectronic devices, chemo/biosensors and the studies of rich physics of 2D superlattices.

A schematic of the fabrication process of 2D graphene superlattice based on the local substrate engineering of graphene chemistry is illustrated in Figure 1b. First, the periodically patterned substrate (PPS) was fabricated by self-assembling monodispersed colloidal SiO₂ nanospheres monolayer onto SiO₂/ Si substrate. Second, chemical vapor deposition (CVD)-grown graphene was transferred onto such patterned substrates. Poly(methyl methacrylate) (PMMA) thin film was used as the transfer medium, and then removed by hot acetone. To introduce periodic compressive strain into the graphene film,

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Figure 1. Graphene superlattice from site-selective chemical reaction. a) Schematic of periodic chemical functionalization of graphene via substrate engineering. b) Experimental procedure for fabricating graphene superlattices. c) Covalent attachment of nitrobenzene groups on graphene basal plane by reaction with diazonium salt. d) Raman spectra of graphene before (blue) and after (red) chemical modification. e) High-resolution XPS N 1s spectra of graphene before (black) and after (red) diazonium reaction, in which the graphene sample was transferred onto a flat 300 nm SiO₂/Si substrate.

thus-obtained samples were annealed at 350 °C for 2 h in forming gas (30 sccm H₂/100 sccm Ar) under atmospheric pressure. Then, the graphene sample was immersed into a 4-nitrobenzene diazonium tetrafluoroborate solution at 40 °C for covalent modification. The following chemical reaction is expected to take place.^[26] The diazonium salt receives electrons from graphene, generating active nitrobenzene free radicals, which attach to the graphene skeleton via covalent bonds (Figure 1c). Finally, the nitrobenzene-terminated graphene superlattice was delaminated from the PPS surface and transferred onto a flat target substrate.

Figure 1d shows the typical Raman spectra of graphene on the PPS before and after chemical modification, revealing the

formation of sp^3 defects. For pristine graphene, no Raman D peak is observed, indicative of its high quality. After the reaction with diazonium salt, a prominent disorder-induced D peak appears at 1350 cm⁻¹ together with a defect-induced D' peak at 1620 cm⁻¹. In addition, the double-resonance 2D peak is strongly weakened. These observations suggest the presence of a large number of sp^3 defects,^[27] which originate from covalent grafting of nitrobenzene groups onto the graphene plane. Further X-ray photoelectron spectroscopy (XPS) study also confirms the reaction between graphene and diazonium salt by revealing an N 1s peak on the modified graphene. As seen from the high-resolution N 1s spectra in Figure 1e, two prominent peaks emerge at 405.8 and 399.7 eV after reaction. The peak at



Figure 2. Graphene superlattice formation on SiO₂ nanospheres assembly. a) SEM image of a graphene sheet on the close-packing monolayer of 150 nm-SiO₂ spheres after thermal annealing. Scale bar: 1 μ m. b) Optical microscope image of graphene sheet after chemical reaction on nanospheres assembly, which was taken after transferred onto a flat SiO₂/Si substrate. Scale bar: 50 μ m. c) SEM image of graphene sheet in (b). The top and bottom insets presented, respectively, the SEM images of graphene sheet annealed on nanospheres assembly without chemical reaction and of that reacted on a flat SiO₂/Si substrate. All the images were taken after transferred onto a flat SiO₂/Si substrate. Scale bar: 1 μ m. d) AFM image of the functionalized graphene sheet shown in (c). Scale bar: 1 μ m. e, f) Histograms of disk height and periodicity distributions of graphene after chemical reaction.

405.8 eV is attributed to the nitro groups, confirming the presence of nitrophenyl groups on the functionalized graphene. The lower binding energy N 1s peak at 399.7 eV is associated with a reduced nitrogen species, possibly generated by transformations from nitro to amine groups caused by electrons used for neutralization in the XPS chamber.^[26] These Raman and XPS results strongly suggest that nitrobenzene groups have been successfully grafted onto the graphene lattice.

Figure 2a shows the scanning electron microscopy (SEM) image of pristine graphene on the closely packed monolayer of 150 nm SiO_2 spheres after thermal annealing. Compressive strain and charge puddles are expected to be introduced into the regions of graphene in close contact with SiO_2 spheres. Figure 2b exhibits the typical optical microscope image of chemically functionalized graphene after delamination from



the PPS surface and transferring onto a flat SiO₂/Si substrate. As is clearly seen, the graphene film keeps its integrity and does not exhibit obvious optical contrast between different areas. However, the SEM image of the same graphene film displayed in Figure 2c is completely different, which is characteristic of a periodic black disk structure with a periodicity matching with the original closepacking nanospheres monolayer. As a control experiment, the same thermal annealing treatment of graphene was done on the nanospheres assembly without chemical reaction. No discernible patterns are observed on graphene sheet in this case (Figure 2c, top inset), which excluded the possible contribution of PPS-induced physical effect after thermal annealing on the pattern formation. In addition, when the same chemical reaction of graphene was done on a flat SiO2/Si substrate, only uniform modification occurred on the whole graphene surface (Figure 2c, bottom inset). The above phenomena suggest that the nanosphere-contacted areas have enhanced the chemical reactivity of graphene with diazonium salt, leading to the site-selective reaction of graphene sheet.

Further atomic force microscopy (AFM) studies confirmed the periodic pattern structure on graphene sheet (Figure 2d). The AFM topographic image exhibits two distinct areas with different heights arranged in a closepacking structure similar to the original PPS pattern. Figure 2e,f gives the statistical distributions of bright disk heights and their periodicities in the AFM image, respectively. The heights differences between two distinct areas fall into a range of 1.6-2.6 nm with a mean value of 2.1 nm. This value is larger than that estimated from one single nitrobenzene group, which is attributed to the formation of nitrobenzene oligomer and the lattice distortion of graphene from sp^2 to sp³ hybridization.^[28] On the other hand, the

periodicity of the nearest neighbor disks falls into a range of 145–170 nm with a mean value of 155 nm. This distance is well consistent with the diameter of SiO₂ spheres (\approx 150 nm) in the closely packed monolayer. Electrostatic force microscopy (EFM) is a direct measurement of the local relative work function with a nanometer scale spatial resolution. EFM was also utilized to characterize the patterned structure on graphene after chemical modification. **Figure 3**a,b presents the AFM and corresponding EFM images of chemically patterned graphene. Obviously, the bright areas in the AFM image have significantly different work functions with the surroundings. The local electrostatic potentials are estimated to be -0.143 and -0.128 V for the bright areas and the surroundings, respectively. This difference in work functions of the two kinds of regions clearly indicates the difference of their chemical natures.

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Figure 3. Origin of graphene superlattices. a,b) AFM and corresponding EFM images of graphene on 150 nm SiO₂ nanospheres assembly after thermal annealing and chemical modification, respectively. The data were obtained after transferred onto flat SiO₂/Si substrates. Scale bar: 500 nm. c) Raman spectra of graphene on nanospheres assembly before (top) and after (bottom) thermal annealing treatment, normalized to the 2D peak height d) Scatter plots of FWHM values of Raman 2D band versus 2D peak position before and after annealing (121 spectra). e) Calculated energy (E_{sc}) and bonding distance (R_{C-C}) changes as a function of strain in graphene.

From the above experimental observations, we conclude that a site-selective chemical reaction has taken place on graphene sheet, originating from the substrate-induced enhancement of chemical reactivity. In other words, the chemical reactivity of graphene can be locally modulated by the structural design of underlying substrate. This offers a straightforward way to fabricate graphene superlattices by using close-packing nanospheres assembly. We can simply change the diameters of $\rm SiO_2$ nanospheres in the assembly to modulate the periodicity of graphene superlattice.

Thermal annealing treatment was found to be critical for fine tuning chemical reactivity of graphene basal plane on the close-packing SiO₂ nanospheres assembly. To investigate the effect of thermal annealing process, Raman spectroscopy was performed to track the annealing process. As shown in Raman spectra of graphene on PPS before and after annealing, the D peak near 1300-1350 cm⁻¹ is very small and does not show any obvious change after annealing (Figure S1, Supporting Information). This observation indicates that no remarkable defects are induced during this annealing process. The G band splits into two peaks: one is similar to the G peak before annealing and the other shows a large upshift along with a broadening (Figure S2, Supporting Information). Figure 3c presents representative Raman 2D band changes of graphene on nanospheres assembly before and after thermal annealing. Before annealing, the 2D peak is centered at $\approx 2689 \text{ cm}^{-1}$, indicating that the pristine graphene is nearly intrinsic graphene.^[29] After annealing and cooling to room temperature, the 2D band splits into two peaks: one is similar to the 2D peak before annealing and the other shows a large upshift of $\Delta_{w2D} = 26 \text{ cm}^{-1}$ along with a broadening. Figure 3d exhibits the statistics results of full width at half maximum (FWHM) of the 2D peak of graphene before and after annealing against its spectral position. The remarkable changes of G and 2D bands are strong evidence of the existence of compressive strain on the graphene plane induced by thermal annealing.^[25,30] Two splitting 2D peaks are corresponding to the suspending areas without mechanical strain and the SiO₂-contacted areas with compressive strain, respectively. The compressive strain arises from the difference in thermal expansion coefficients between graphene and the underlying SiO₂ spheres.^[25] As the temperature increases, graphene contracts while the underlying SiO₂ spheres expand. On the other hand, graphene expands while the underlying substrate shrinks in the cooling process. Relative slipping occurs between the graphene sheet and the substrate over a critical temperature, determined by van der Waals forces between them. Local compressive strain remains in the graphene plane at the SiO₂ nanosphere-contacting areas, as evidenced by the above Raman 2D band changes.^[30] In addition, the SiO₂-contacted graphene has much larger FWHM of 2D band than suspended one. The larger FWHM of 2D band might be contributed to the presence of electron-hole puddles on SiO₂-contacted graphene because electron-hole puddles on graphene whose size is smaller than Raman laser spot size would lead to a broader 2D band.^[18]

We theoretically calculated the strain effect on the chemical reactivity of graphene based on the following formulas

$$\begin{split} E_{\rm b} &= E_{\rm CMG} - (E_{\rm G} + E_{\rm CF}) \\ E_{\rm sc} &= E_{\rm b}^{\sigma} - E_{\rm b}^{0} = \left(E_{\rm CMG}^{\sigma} - E_{\rm CMG}^{0} \right) - \left(E_{\rm G}^{\sigma} - E_{\rm G}^{0} \right) \end{split}$$

where $E_{\rm b}$ is the binding energy, $E_{\rm G}$ is the energy of graphene, $E_{\rm CMG}$ is the energy of chemically modified graphene, $E_{\rm CF}$ is the energy of the functional group, and $E_{\rm sc}$ is the difference of the reaction energy between graphene with and without strain. The superscripts σ and 0 denote the value with and without isotropic strain on graphene, respectively. Figure 3e shows the change of $E_{\rm sc}$ value as a function of strain on graphene. Apparently, $E_{\rm sc}$ decreases for both tensile and compressive



strains, indicating that graphene under strain is more energetically favorable for chemical reactions as expected. At a strain less than 0.02, there is no distinct difference between tensile and compressive strains on graphene's reactivity. At a larger strain, however, the compressive strain is more effective for enhancing the reactivity ($E_{sc} = -1.65$ eV for $\sigma = -0.05$; $E_{\rm sc} = -0.21$ eV for $\sigma = 0.05$). In addition, as the compressive strain increases, the distance between graphene and functional group gradually decreases. This theoretical result well supports our experimental observation, i.e., the local compressive strain induced by SiO₂ nanospheres can enhance the chemical reactivity of graphene with diazonium salt. Thus, the compressive strain combined with charge puddles enhanced and differentiated SiO2-contacted graphene's reactivity from the surroundings, enabling the mask-free chemical patterning of graphene.

Various graphene superlattices can be fabricated by designing the supporting substrates of graphene sheet based on this local substrate-induced chemical reaction approach. The periodicity of graphene superlattice can be simply modulated by varying the diameters of SiO₂ nanospheres. Graphene superlattices with a periodicity of 400 (Figure 4e), 150 (Figure 4f), and 114 nm (Figure 4g) have been fabricated in such a way. By using a SiO₂ nanohole array substrate shown in Figure 4d, a graphene superlattice with reversed pattern structure has been successfully fabricated (Figure 4h). It should be emphasized that the control of reaction time is critical to the formation of superlattice. Taking a 150 nm SiO₂ nanospheres assembly as the supporting substrate, we gradually increased the reaction time of graphene with diazonium salt from 0.5 to 4 h. At the beginning, no discernible pattern structure was observed (Figure 4i). The graphene superlattice appeared after 1 h reaction (Figure 4j). However, an over-reaction also destroyed the superlattice structure as seen in Figure 4k. The reason is that the reaction has occurred on the whole graphene surface in an elongated reaction time. Moreover, there is also a big freedom for grafting different functional groups onto graphene sheet using the presented approach. Given in Figure 4l is an example of graphene superlattice made by photomethylation reaction, in which graphene was periodically modified by methyl groups instead of nitrobenzene.

In summary, we present a universal substrate engineering approach to fabricate graphene superlattices based on the substrate-enhanced chemical reactivity of graphene. Various graphene superlattices down to nanometer scale have been made by using the close-packing monolayer of SiO₂ nanospheres with different periodicities. It has been proved that such a strategy can be applied to fabricate arbitrary graphene superlattices simply by nanostructuring the supporting substrates of graphene sheets. There is also a freedom for the choice of chemical reactions, as demonstrated by diazonium salt reaction and photomethylation reaction in this work. This allows us to make a periodic modification of graphene sheet with desired functionalities. This mask-free technique provides an effective and versatile route for fabricating graphene superlattice which can be utilized in graphene-based electronic and optoelectronic devices, chemo/biosensors and for studying the rich physics of 2D superlattices.



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Figure 4. Versatile graphene superlattices. a–c) SEM images of 400, 150, and 114 nm SiO₂ nanospheres assembly used for superlattice formation, respectively. d) SiO₂ nanohole array with a periodicity of 200 nm used for superlattice formation. e–h) Graphene superlattices made from (a–d) after reacting with diazonium salt and transferred onto flat SiO₂/Si substrates. i–k) SEM images of graphene sheet on 150 nm SiO₂ nanospheres assembly with a reaction time of 0.5, 1, and 4 h, respectively. I) SEM image of graphene superlattice obtained from 150 nm SiO₂ nanospheres assembly by photomethylation reaction. The scale bars in (a–c) and (e–g) are 500 nm, and in (d), (h–l) are 200 nm, respectively.

Experimental Section

Preparation of PPS: Aminopropyl methyl-diethoxysilane was added to a stock solution containing 1 wt% monodisperse colloidal SiO₂ nanospheres (Unisize Technology, China). After heating the solution to 100 °C for 8–12 h, the resulting solution was washed three times with ethanol and then ultrasonicated in methanol. Then, the chemically modified SiO₂ spheres were self-assembled onto SiO₂/Si substrates by using Langmuir–Blodgett technique. The SiO₂ nanohole array substrate was fabricated through the following procedures: commercial polyethylene spheres were deposited onto SiO₂/Si substrate to form a close-packing monolayer; then the spheres were shrunk down by plasma etching treatment; a 10 nm SiO₂ layer was thermally deposited onto the substrate and the spheres were removed after ultrasonic treatment in toluene. Before transferring graphene onto PPS, the as-prepared PPS was treated with oxygen plasma for 30 min (15 W) to remove organic components on the sphere surface.

Site-Selective Modification of Graphene: The CVD grown graphene on Cu foils was transferred onto PPS by using a "dry transfer" $\mathsf{method}^{[31]}$ to avoid water trapping between graphene and substrate. After transferring the graphene film onto PPS, the sample was annealed at 350 °C for 2 h in forming gas (30 sccm $\rm H_2/100$ sccm Ar) under ambient pressure. Then, the graphene samples were immersed into a mixed aqueous solution of 20 mm 4-nitrobenzene diazonium tetrafluoroborate (≈10 mL) and 1 wt% sodium dodecyl sulfate aqueous solution (2 mL), where they were reacted for 1.5 h at 40 °C. For the photomethylation process, the graphene samples were immersed in di-tert-butyl peroxide (99%) and irradiated under UV light with the wavelength range from 320 to 500 nm. After site-selective chemical modification, the samples were rinsed with deionized water, immersed in deionized water for 2 h, and dried with nitrogen gas. To nondestructively delaminate the functionalized graphene film from PPS, the samples were immersed in a 10% HF aqueous solution at room temperature using PMMA film as the transfer medium. After

detaching the graphene from PPS, we left the PMMA-supported graphene floating in HF solution for 20 min before transferring it to flat SiO_2/Si substrates for completely removing the residual SiO_2 . The PMMA film was finally removed by hot acetone.

Characterizations: Raman spectra were collected with a Horiba Jobin Yvon Lab RAM HR800 system with a 514.5 nm excitation laser. The laser spot size was $\approx 1 \ \mu$ m. XPS measurements were performed on a Kratos Axis Ultra spectrometer with Al K α monochromated radiation at low pressures of 5×10^{-9} – 1×10^{-8} Torr. The XPS collection area was $\approx 300 \times 700 \ \mu$ m². To correct for charging, the highest peak in C 1s spectrum was shifted to 284.5 eV. AFM and EFM were conducted on a Bruker Dimension Icon atomic force microscope in tapping mode. For EFM measurements, the topographic information was obtained in the first pass, and then the tip was lifted by a given constant height of 20 nm above the sample surface and biased a DC voltage V_{tip} in the second pass. Conducting tips (SCM-PIT, Bruker) with a resonance frequency of ca. 70 kHz and spring constant of ca. 2.8 N m⁻¹ were used.

Theoretical Calculations: To perform geometry optimization and energy calculations for graphene and chemically modified graphene under different strains, density functional theory implemented in the Vienna ab initio simulation package^[32] was used. Considering spin polarization, we adopted the general gradient approximation with the Perdew–Burke–Ernzerhof exchange correlation functional^[33] and a cut-off energy of 520 eV. Geometry optimization continued until all the atomic forces were less than 0.01 eV/Å. The Monkhorst–Pack grid mesh was $7 \times 7 \times 1$ for all systems in the self-consistent field iteration. Adjacent sheets were separated by at least 20 Å to avoid interactions between them.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



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