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Graphic Abstract

One-step growth of reduced graphene oxide for low cost high performance electronics and optoelectronics

One-Step Growth of Reduced Graphene Oxide on Arbitrary Substrates

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Abstract:

Reduced graphene oxide (rGO) has inherited the outstanding electronic, optical, thermal and mechanical properties of graphene to a large extent, while maintaining sufficient chemically active sites. Therefore, it has attracted a great deal of research attention in the fields of energy storage, electronics, photonics, catalysis, environmental engineering, etc. Currently, the most popular way to prepare rGO is to reduce graphene oxide, which is obtained by modified Hummer methods using tedious treatments in a harsh environment, to rGO flakes. Industrial applications demand advanced preparation methods that can mass produce highly uniform rGO sheets on arbitrary substrates. In this work, a one-step growth process is introduced that utilizes cellulose acetate as a precursor, without any catalysts, to produce uniform ultrathin rGO films on various substrates and free-standing rGO powders. Systematic spectroscopic and microscopic studies on the resulting rGO are performed. Prototypes of electronic and optoelectronic devices, such as field effect transistors (FETs), photodetectors, and humidity sensors, are fabricated and tested, demonstrating the intriguing applications of our rGO materials across a wide range of fields.

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1. Introduction

Reduced graphene oxide (rGO) has attracted a great deal of attention from researchers thanks to its anticipated applications in transparent and flexible electronics,^{1,2} supercapacitors,³ batteries,⁴ sensors,⁵ photodetectors,⁶ electromagnetic shielding,⁷ etc. It possesses higher in-plane electrical conductivity than graphene oxide (GO) and contains more active sites (e.g., hydroxyl groups and defects) for chemical functionalization and catalysis than pristine graphene.⁸⁻¹¹ Currently, modified Hummers' methods are the most popular way to prepare GO and its derivatives, such as rGO.¹⁻¹² Briefly, graphite is oxidized and intercalated using a mixture of potassium permanganate (KMnO₄), NaNO₃, and concentrated H₂SO₄. The product is purified to obtain GO. Then, an aqueous dispersion of the obtained GO is treated with reducing agents, such as a solution of hydrazine and ammonia, to partially restore the graphitic sp² carbon. Finally, these rGO dispersions have to be transferred onto target substrates via spray or filtration for thin-film applications. Due to the strong oxidizers and various reducing agents involved in these processes, it is difficult to control the size, roughness, and thickness of the end rGO product. In this work, we report a facile way of growing ultrathin rGO films on arbitrary substrates and free-standing rGO powders, where the solid precursor (cellulose acetate) is transformed by thermal annealing. Regarding the selection of solid precursors, small organic molecules such as glucose need to go through polymerization process under certain conditions to form oxygen-containing polymers first before transformed into rGOs, otherwise they will sublime away completely under vacuum at high temperature. Therefore, in our procedure of one-step growth of rGO, polymers such as cellulose acetate are our first choice considering the cost, simplicity and practicability. Here, we refer to rGO derived from cellulose acetate as CA-rGO. Cellulose acetate is an ester of cellulose, which is abundant in natural resources such as cotton, wood, and hemp. It can be readily dissolved in a wide range of solvents, such as acetone, dioxane, and methyl acetate,^{13,14} and spin-

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coated onto arbitrary substrates, which has facilitated its use in both academic and industrial applications.¹⁴⁻¹⁶

2. Experimental

2.1 Cellulose acetate spin-coating parameters and CA-rGO growth conditions. Generally, the target substrates (quartz, SiO₂/Si, Cu, Si, glass etc.) were spin-coated with a 10 mg/mL cellulose acetate (Sigma Aldrich, average Mn ~ 30,000 by GPC) solution in acetone at 5,000 rpm for 60 s. The spin-coated device was loaded into a quartz tube inside a self-assembled Chemical Vapor Deposition (CVD) system. Then, pressure in the tube chamber was pumped down to high vacuum (1 mtorr). At room temperature, 50 sccm H₂ and 250 sccm Ar were introduced into the tube chamber to maintain a constant pressure of 10 torr. The furnace temperature was increased to 1040 °C (600 °C for glass substrates) over 30 min and kept at 1040 °C (600 °C for glass substrates) for 1 hr, after which the chamber was cooled down to room temperature quickly by airflow. At high temperatures (1040 °C), by adjusting the growth parameters, small flakes of graphene (~ 4 μm²) can be obtained on Cu. However, for other substrates, CA-rGO is the common product under most circumstances, and large area graphene with prominent 2D peak in the Raman spectroscopy has never been observed without metal catalysts.

2.2 Raman spectroscopy and mapping. Raman spectra and mapping of rGO of CA-rGO grown on 300 nm SiO₂/Si substrates were recorded using a Renishaw inVia confocal Raman microscope with a 532 nm laser. The Raman mapping area was 10 μm x 10 μm.

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2.3 Atomic force microscopy (AFM). Atomic force microscopy (AFM) images of CA-rGO grown on 300 nm SiO₂/Si substrates were collected on an Agilent 5400 SPM in tapping mode.

2.4 UV-vis-NIR spectroscopy. The absorption spectra of a 20 nm thick CA-rGO thin film grown on a quartz substrate was collected on a Varian Cary 5000 in the Analytical Chemistry Core Lab at KAUST.

2.5 Thermogravimetric analysis (TGA). TGA of CA-rGO powders was performed in air at a 1 °C /min heating rate with a NETZSCH STA 449 F3 Jupiter.

2.6 Infrared spectroscopy (IR). Infrared spectroscopy of CA-rGO grown on a quartz substrate was recorded using a Nicolet IS10 FT-IR spectrometer (Thermo Fisher Scientific) in the Analytical Chemistry Core Lab at KAUST.

2.7 X-ray photoelectron spectroscopy (XPS). XPS data of CA-rGO and cellulose acetate on Au thin films were collected in a Kratos Supra spectrometer, armed with a monochromatic Al K α x-ray source ($h\nu = 1486.6$ eV), in a high vacuum using an aperture slot of 300 $\mu\text{m} \times 700$ μm .

2.8 High-Resolution Transmission electron microscopy (HRTEM). The CA-rGO samples were first grown on Cu foil (Alfa Aesar, 99.8%) and then transferred onto a 400 mesh Cu transmission electron microscopy (TEM) grid (Pacific Grid Tech, Cu-400HD) using a clean

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graphene-transfer method previously reported in the literature.¹⁴ High-resolution transmission electron microscopy (Titan 80-300, FEI) was used to record the images.

2.9 Field effect transistors (FETs). A 20 nm thick CA-rGO film was grown on a 300 nm SiO₂/Si substrate. Then, photolithography, plasma etching, and sputtering were performed on the film to create 50 μ m x 50 μ m FET devices (Figure 1e, left). The device contacts were 10 nm Ti/100 nm Au. Transfer characteristics of FETs were measured with a probe station (Eeverbeing Int'l Corp.).

2.10 Photodetector and humidity sensors. For each CA-rGO device, ninety interdigitated Ti/Au (10/100 nm) electrodes with a 40 μ m electrode width, 40 μ m electrode separation, and 8.8 mm electrode length were prepared on quartz substrate by nanofabrication. The resulting channel width to length is 19,800. Then Photolithography defined cellulose acetate square (9 mm x 9 mm) on top of interdigitated electrodes was reacted into CA-rGO under the same condition described above, except that the reaction temperature is 850 °C instead of 1040 °C in order to protect the electrodes. The measurements of the CA-rGO photodetector were taken inside glovebox using a Keysight B2912A sourcemeter and LEDs with different wavelengths from Thorlabs. The LEDs were supplied with a Tektronix AFG3252 function generator for transient photoresponse measurements. The area of the aperture for illumination was 25 mm². The effective photoresponse R_E is calculated as follows:

$$\varepsilon = \frac{\text{Device Area}}{\text{Illuminated area}} = \frac{9 \times 9}{25/2} = 6.48$$

$$R = \frac{\sigma - \sigma_0}{\sigma}$$

$$R_E = R \cdot \varepsilon$$

where ε is the effective photoresponse coefficient, σ is the conductivity of CA-rGO film under illumination, σ_0 is the conductivity of CA-rGO film right before illumination, R is measured photoresponse and R_E is the calculated effective photoresponse.

The measurements of CA-rGO humidity sensor were collected in a homemade gas chamber, where the humidity was controlled by introducing flowing N_2 through a bubbler into the chamber. The current was measured using the Keysight B2912A sourcemeter, and humidity was measured using the HTM2500LF temperature and humidity module from Measurement Specialties. All the instruments were controlled with a data acquisition card and MATLAB software.

3. Results and Discussion

3.1 One-step growth process of CA-rGO. Here, we synthesized the cellulose acetate derived rGO (CA-rGO) by direct thermal annealing of the cellulose acetate polymer under a continuous flow of H_2/Ar . In a typical experiment, we spin-coated the target substrate (quartz, SiO_2/Si , Cu, etc.) with an acetone dispersion of cellulose acetate (Figure 1a,b) and then transferred to a CVD furnace to grow CA-rGO at a high temperature (Figure 1c,d). The solution of cellulose acetate exhibits Tyndall effect under a beam of red laser (635 nm), suggesting the fine particles of cellulose acetate polymer were well dispersed in acetone. The thickness of a cellulose acetate film can be precisely mediated by the concentration of cellulose acetate dispersion and the spin parameters (time, speed, acceleration, etc.). CA-rGO can be grown in the form of both films and

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powders: a CA-rGO film-based FET device fabricated on a 300 nm SiO₂/Si substrate and an as-grown, free-standing CA-rGO powders are shown in Figure 1e (left and right, respectively). Also, catalysts are unnecessary; therefore, CA-rGO can be grown on arbitrary substrates. Figure 1f displays the proposed chemical structure of CA-rGO, which we established through the following characterization studies.

Figure 1 | One-step growth of CA-rGO. (a) A 10 mg/mL acetone solution of cellulose acetate showing the Tyndall effect. (b) Chemical structure of cellulose acetate. (c) Schematic of the CVD setup. (d) CA-rGO growth condition. (e) Microscope images of a CA-rGO FET device and as-grown CA-rGO powders. (f) Proposed chemical structure of CA-rGO.

3.2 Spectroscopy analysis of CA-rGO. Raman spectroscopy is a very sensitive and nondestructive tool for characterizing carbon nanomaterials, especially graphene and its derivatives.¹⁷⁻²¹ Figure 2a compares the Raman spectra of CA-rGO film with the precursor, cellulose acetate film, before and after chemical reactions under different conditions. Before the reaction, the pure cellulose acetate shows no obvious peak in the Raman spectrum range 1050-1950 cm⁻¹. However, after a chemical reaction at 1040 °C for 1 hour, CA-rGO was obtained as evidenced by the high D-peak at ~1367 cm⁻¹, the prominent G-peak at ~1619 cm⁻¹, the suppressed 2D-peak (~2680 cm⁻¹), the D+D'-peak (~2944 cm⁻¹) and the 2D* peak (~3219 cm⁻¹)

(Figure 2a, S1a). The presence of 2D peak and D+D' peak indicates the generation of the electronic π conjugation and thus good graphitization during the growth process. The G mode of graphitic materials is ascribed to E_{2g} symmetry, and unlike D mode, the activation of G mode does not require defects.^{16,22} The blue shift of the G-peak in CA-rGO ($\sim 1619\text{ cm}^{-1}$) compared to pristine CVD graphene ($\sim 1584\text{ cm}^{-1}$) was attributed to the presence of nanocrystalline graphene in the CA-rGO samples because the merge of D' peak with G peak in small grain graphene can result in the upshift of G peak.^{20, 21} We also observed that the full width at half maximum (FWHM) of the D peak increased as the H_2 percentage decreased. The D peak is related to the A_{1g} breathing mode, and is activated by disorders in graphene. The blue shift of the D peak in CA-rGO compared to pristine graphene may come from the small-size graphene domains in CA-rGO.²¹ The I_D/I_G ratio is widely used to characterize graphitization in carbon materials. Generally speaking, the better the graphitization, the smaller the I_D/I_G ratio. A higher percentage of H_2 gas, restored the sp^2 carbon to a large extent and, therefore, resulted in a smaller D peak as shown in Figure 2a. We note that the height of the D peak was higher than the G peak in CA-rGO, consistent with previously reported Raman spectra of rGO produced by modified Hummer methods.^{11,23} In intensively oxidized graphene oxide, on the other hand, the literature reports that the height of D peak is lower than the G peak.^{20,24-26}

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Figure 2 | Spectroscopy analysis of CA-rGO. (a) Raman spectra of cellulose acetate before (black) and after (red, blue, and purple) chemical reactions under different conditions. FT-IR spectra (b) and UV-vis spectra (c) of a 20 nm CA-rGO thin film grown on a quartz substrate. (d) Thermogravimetric analysis of CA-rGO powders in air. C 1s (e) and O 1s (f) XPS spectra of as-grown CA-rGO thin films on Au substrates.

To appreciate the functional groups in CA-rGO, we performed mid-infrared spectroscopy on 20 nm CA-rGO thin films on a quartz substrate. Normally, rGO samples are graphene functionalized with oxygen-containing groups found at the edges or in the defects of the basal plane.^{1,26} Figure 2b illustrates the presence of a C-O (phenolic) stretching vibration peak at 1055 cm⁻¹, a C=C (sp² hybridized carbon) skeletal vibration peak at 1631 cm⁻¹, a C=O stretching vibration peak at 1730 cm⁻¹, C-H stretching vibration peaks at 2848 cm⁻¹ and 2917 cm⁻¹, and an O-H vibration peak at 3297 cm⁻¹. The pronounced C=C peak and weak C-O and C=O stretching vibrations announce the graphene-like electronic structure of these samples, distinguishing them as rGO and not GO. Interestingly, prominent peaks corresponding to C-H vibrations are

observed in CA-rGO samples, suggesting that some of their edges terminated with hydrogen. A broad and evident peak related to a hydroxyl group is rare in rGOs derived from GO using modified Hummer methods. The enrichment of these O-H groups suggests possible applications of CA-rGO in humidity sensors, because CA-rGO contains higher in-plane conductivity than GO and more O-H groups than either traditional rGOs or graphene.

The UV-vis spectra of the 20 nm thick CA-rGO film showed a weak absorbance of wavelengths within the 200 nm-800 nm range due to ultrathin thickness, with a peak at ~250 nm that corresponded to the $\pi \rightarrow \pi^*$ transitions. Since oxygen-containing covalently functionalized chemical groups exist in CA-rGO film, we assigned the blue shift of this peak in the CA-rGO film compared to that of pure graphene nanoplatelets (~270 nm) to its incomplete graphene-like electronic structure.^{20,27} The absorbance coefficient at 660 nm is calculated to be $1.5 \times 10^4 \text{ cm}^{-1}$.

The thermal property of CA-rGO powders was investigated by TGA in air (Figure 2d). The TGA curve of CA-rGO resembles that of graphene²⁸. Before 500 °C, only 2% weight loss is observed, which indicates that the oxygen containing takes up about 2% weight of CA-rGO. After 500 °C, the sp^2 carbon of CA-rGO starts to be oxidized. The fastest weight loss appears at 661°C.

The elemental composition of CA-rGO was further analyzed by X-ray photoelectron spectroscopy (XPS). The spectra of cellulose acetate and CA-rGO on Au film from the XPS survey can be found in Supplementary Figure S2a. Only carbon and oxygen elements were detected in both samples, suggesting high purity of CA-rGO. The O/C ratio in cellulose acetate was calculated to be 0.53, which reduced to 0.01 after graphitization, as shown in the CA-rGO survey spectra, indicating that the oxygen content drastically decreased after the reaction. The C

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1s core level from cellulose acetate (shown in Figure S2b) was fitted using four components, located at 285.0 eV, 286.4 eV, 287.5 eV, and 288.9 eV, corresponding to the C-C/C-H (sp^3), C-O/C-OH, O-C-O, and O-C=O bonds, respectively. The O 1s core level (shown in Figure S2c) from cellulose acetate was fitted using three components, located at 531.9 eV, 532.7 eV, and 533.4 eV, corresponding to the O-C=O, O-C-O/C-OH, and O-C=O bonds, respectively.²⁹ The XPS intensity ratio of the O-C=O peak to the O-C-O peak was about 2:1, consistent with the chemical structure shown in Figure 1b. Figure 2e gives the high resolution XPS spectra of the C 1s core level from CA-rGO. The C 1s core level was fitted using six components, located at 284.4 eV, 285.0 eV, 286.4 eV, 288.0 eV, 289.2 eV, and 290.6 eV, corresponding to the C=C (sp^2), C-C/C-H (sp^3), C-O/C-OH, C=O, and O-C=O bonds, and to the $\pi-\pi^*$ shake-up satellite-structure characteristic of a conjugated system, respectively.^{25,30-33} The C 1s spectrum is dominantly from graphitic carbon, confirming that the sp^3 carbon in cellulose acetate has been turned into sp^2 carbon in CA-rGO after the reaction. The O 1s core level in Figure 2f was fitted using three components, located at 532.0 eV, 532.6 eV, and 533.7 eV, corresponding to the O-C=O, C=O /C-OH, and O-C=O bonds, respectively. The oxygen level in CA-rGO was estimated to be 1%, which is much lower than regular graphene oxide.^{23,26} The XPS characterizations provide further evidence that the product is rGO in nature, instead of GO.

3.3 Microscopy analysis of CA-rGO. We carried out AFM measurements to investigate the morphology of our materials before and after the reaction. Figure 3a displays AFM image of a spin-coated cellulose acetate film with porous structures. We estimated the average pore size (diameter) and wall thickness between adjacent pores to be ~140 nm and ~70 nm, respectively. After the reaction, randomly but uniformly distributed and interconnected CA-rGO nanoplatelets

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(~50 nm in diameter) were formed (Figure 3b). Figure S3a-c and Figure 3c-f show HRTEM characterization of CA-rGO with increasing magnification. The CA-rGO thin film was first grown on Cu foils and then transferred to a TEM grid following a previously reported clean graphene-transfer method.^{22, 34} Figure 3c shows that the CA-rGO nanoplatelets were densely packed and interconnected with each other. Interestingly, in some areas the separated CA-rGO islands were connected to each other by graphene-like thin films (red circle). Raman mapping of the D peak (Figure S1b) further proved that the interconnected area (black) had a lower D peak, indicating a graphene-like structure. Figure 3d illustrates that the CA-rGO nanoplatelets were polycrystalline with an approximate domain size of 10 nm x 10 nm. A small defective area, identified by a black square in Figure 3e, is magnified in Figure 3f, where the carbon atoms are indicated by white dots. The typical honeycomb-lattice structure of multilayer graphene with an AB stack between the adjacent layers can be clearly observed. The C=C bond distance in CA-rGO was measured to be 0.152 nm, consistent with the literature.³⁵⁻³⁷

Figure 3 | Microscopy analysis of CA-rGO. (a) AFM image of a 5 μm x 5 μm spin-coated cellulose-acetate film (inset, 1 μm x 1 μm). (b) AFM image of a 5 μm x 5 μm CA-rGO thin film grown on a 300 nm SiO_2/Si substrate (inset, 1 μm x 1 μm). (c-f) HRTEM images of CA-rGO thin films under increasing magnification.

3.4 CA-rGO electronic and optoelectronic devices. Measurements of the FET transfer characteristics (Figure S4a) from our CA-rGO devices show a p-type transistor, which is due to the functionalized hydroxyl groups in CA-rGO and the dopants from air. Note that the resistance at 0 voltage was calculated to be 15.7 M Ω (corresponding electrical conductivity $\delta = 0.0157$ S/m), which we attributed to the nanoscale dimensions and a poor interconnection among the CA-rGO nanoplatelets. The junction conductance of CA-rGO may get improved by organometallic chemistry as previously reported in the case of graphene^{20,38,39} and single-walled carbon nanotubes,^{40,48} which is beyond the scope of this work. An AFM height profile was collected from the FET device (Figure S4b). It shows that the average thickness of the CA-rGO film is ~ 20 nm, which gives a large surface area of these films and facilitates the application of

CA-rGO as a competitive sensor material. The abrupt peak around 6 μm is probably due to the turnover of the edges of the film device (Figure S4b inset) during photolithography process.

As mentioned above, rGO has a lot of fascinating applications in sensors, photodetectors, electromagnetic shielding, paints, etc. In this study, we fabricated large-area CA-rGO thin film devices grown on top of interdigitated electrodes (Figure 4a,c) and tested their performances as both photodetectors (Figure 4b) and humidity sensors (Figure 4d).

The CA-rGO photodetectors responded quickly to both UV and visible lights (Figure 4b). The CA-rGO devices responded fast to both white light and UVA (365 nm) light at a frequency of 0.05 Hz, faster than most rGO photodetectors^{41,42} and single-walled carbon nanotube/ZnO heterostructure based photodetector⁴³ reported in the literature as shown in Table S1. Also, the CA-rGO devices were twice as sensitive to white light as to UVA light, which is probably due to the photoresponse of rGO to a wide light spectrum, from infrared to ultraviolet.^{41,42, 44,45} The performance of the devices could be further improved by chemical functionalization, band-gap engineering⁴⁶, or by combining other 2D materials to create heterojunctions.

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Figure 4 | CA-rGO-based electronic devices. (a) Schematic of the setup for CA-rGO photoresponse measurements. (b) Effective photoresponses of a 20 nm thick CA-rGO thin film on quartz to white light (red curve) and UVA light (365 nm, blue curve). (c) Schematic of the setup for CA-rGO humidity sensing measurements. (d) Normalized response of a 20 nm thick CA-rGO humidity sensor to a humid air flow.

The 2D nature, abundant hydroxyl groups, and sufficient chemically active sites of CA-rGO lead to promising sensing devices. Here, we demonstrated the notable responses of CA-rGO devices to a modulated humid flow, with a humidity varying from 16%-62% (Figure 4d). This is

the limit of the humidity inside our self-assembled sensing system. The response was normalized in regard to the conductance measured at low humidity (G_L) and at high humidity (G_H): $G_N = (G - G_L)/(G_H - G_L)$.

The response time of CA-rGO devices was ~ 100 s and the recovery time was ~ 8 s, which is comparable to the previous reported rGO humidity sensors.^{46, 47} We believe that with further optimization of the film thickness, experimental setup, dopants (N, F), and functionalized groups, ultrafast CA-rGO sensors can be obtained in the future.

4. Conclusions

We demonstrated a one-step growth of CA-rGO from cellulose acetate on arbitrary substrates, which is far simpler than the traditional processes for preparing rGO. The size of the CA-rGO nanoplatelets and their extent of graphitization can be mediated by controlling the reaction temperature and the percentage of H_2 in the reductive gas mixture. The graphene-like in-plane crystalline structure of our CA-rGO thin film, along with its abundant chemically active sites (hydroxyl groups and defects) and large surface area, enabled the fabrication of high-performance photodetectors and humidity sensors.

This one-step growth method also allowed us to dope CA-rGO directly during the grow process with transition metals, such as Ag and Cu, to introduce antibacterial properties relevant for applications in wastewater treatment, which will be studied in our future work.

Last but not least, the annual global production of cellulose acetate materials such as thermoplastics reached 800,000 tons in 2008, and many of these products are not recycled.⁴⁹ Our study provides a facile route to convert this cellulose acetate refuse into valuable rGO sensors, photodetectors, and electromagnetic shielding materials. Ultimately, this may reduce the cost of

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rGO-based devices and mitigate the damage to our living environment from cellulose acetate production.

Data availability. The data related to this study are available from the corresponding authors upon request.

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Additional information

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