

Laser-Engineered Multifunctional Graphene–Glass Electronics

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Glass electronics inspire the emergence of smart functional surfaces. To evolve this concept to the next level, developing new strategies for scalable, inexpensive, and electrically conductive glass-based robust nanocomposites is crucial. Graphene is an attractive material as a conductive filler; however, integrating it firmly into a glass with no energy-intensive sintering, melting, or harsh chemicals has not been possible until now. Moreover, these methods have very limited capability for fabricating robust patterns for electronic circuits. In this work, a conductive ($160 \text{ O}\Omega \text{ sq}^{-1}$) and resilient nanocomposite between glass and graphene is achieved via single-step laser-induced backward transfer (LIBT). Beyond conventional LIBT involving mass transfer, this approach simultaneously drives chemical transformations in glass including silicon compound formation and graphene oxide (GO) reduction. These processes take place together with the generation and transfer of the highest-quality laser-reduced GO (rGO) reported to date (Raman intensity ratio $I_D/I_G = 0.31$) and its integration into the glass. The rGO-LIBT nanocomposite is further functionalized with silver to achieve a highly sensitive (10^{-9} M) dual-channel plasmonic optical and electrochemical sensor. Besides the electrical circuit demonstration, an electrothermal heater is fabricated that reaches temperatures above 300°C and continuously operates for over 48 h.

is making it possible to interact with everything around us and experience our habitat in new seamless ways. A perfect example of these advancements is smart surfaces that can perform multiple functions simultaneously—from displaying information about their surroundings to performing actions without human interference based on what is happening inside those walls. The fundamental challenge is integrating electronic circuits, sensors, and actuators into conventional surfaces. These omnipresent materials include polymers, ceramics, metals, and especially glass, which is ideal for multifunctional electronics due to its electrical insulation and optical transparency.

Glass can be coated with electrically conductive oxides, metals, or carbon nanomaterials for optoelectronics and solar,[1–5] while graphene and its derivatives are especially great additives because of their remarkable optical, mechanical, and electrical properties.[6–9] Notably, except for coatings, graphene could be added to different substrates following a wide range

of transfer methods like polydimethylsiloxane stamping, poly(methyl methacrylate) (PMMA)-assisted transfer, electrochemical, roll-to-roll, and laser-assisted transfer.[10,11] These strategies have unavoidable drawbacks: mechanical exfoliation

1. Introduction

Integrating electronics into everyday objects is revolutionizing the way we live our lives. The Internet of Things' emergence

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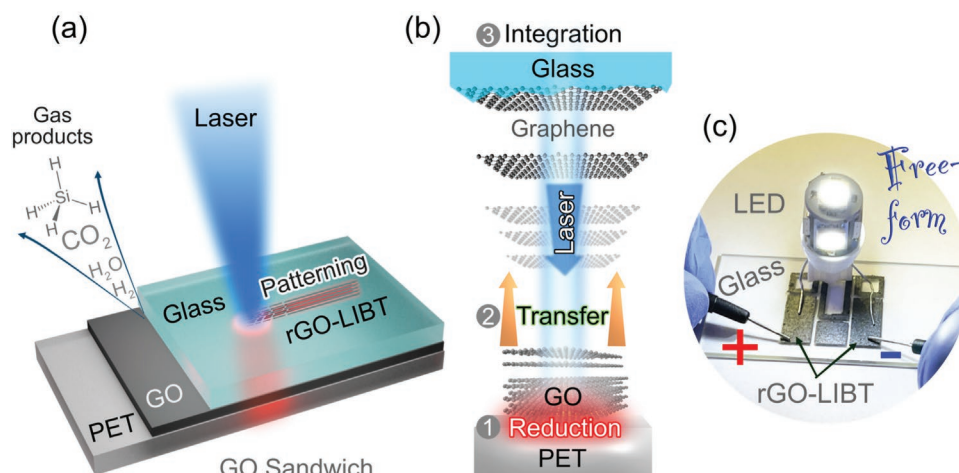


Figure 1. a) Illustration of the laser-induced graphene–glass composite by LIBT. A GO film is deposited on a PET substrate and then covered by a glass target. This GO sandwich is then laser-irradiated from the top. b) During irradiation, the simultaneous GO reduction and H₂O and CO₂ gas release (1), graphene transfer (2), and its integration into the glass (3). c) These three processes in a single laser-processing step allow creating free-form glass electronics. The picture shows an actual LED-powered through a free-form rGO-LIBT glass circuit.

suffers from low yield and unwanted glue leftovers;^[12] PMMA film-assisted transfer also requires extensive residue cleaning; electrochemical ones result in mechanical deformation and undesired doping;^[13] and finally, roll-to-roll technology is limited to flexible substrates.^[14] Moreover, none of these strategies allow integration to glass but only physical transfer resulting in films with low mechanical robustness. There are previous reports on producing graphene/glass composites based on mixing graphene with glass (graphene distributed in the bulk matrix).^[15] Those approaches do not allow forming a resilient composite selectively on the glass surface but change the whole glass volume. Thus, intrinsic glass properties and structural integrity at the bulk of the material are affected.

In this context, this work aims at using laser processing to unlock our ability to form mask-free arbitrary-shaped electrical circuits with the highest reduced graphene oxide (rGO) quality embedded into the glass surface. We postulate that the laser transfer approach is more strategic^[16] for glass electronics since it is easy to perform, eco-friendly, inexpensive, and scalable.^[17–19] This approach combines the integration of rGO into a glass while simultaneously inducing chemical transformations in both materials. Those transformations are the reduction of graphene oxide and propelling the most reduced and thinnest layers to glass on the one hand. On the other hand, photoinduced reactions with glass result in silanes and silicon carbide formation due to high temperatures and carbon from graphene oxide (GO). These spatially-localized chemical processes yield high-quality graphene and reduction of glass to silicon, allowing creating conductor/semiconductor layered structures within a single-step processing cycle. Another crucial advantage of laser-driven transfer is that it could spatially control the electrically conductive regions with high precision. This free-form patterning capability has far-reaching implications for device design.^[20] For instance, with the help of direct laser processing^[21] or laser-induced forward transfer, one could integrate graphene,^[22] its derivatives,^[23,24] or metal nanoparticles^[25] into polymers. Laser reduction of GO showed back in 2009 became

a widespread strategy to make conductive arbitrary-shaped patterns.^[26] However, this and other similar approaches reported up to now do not result in robust nanomaterial integration into the glass. This work aims to overcome this issue using the laser-induced backward transfer (LIBT), first demonstrated by Praeger et al.^[27] A LIBT-based approach can be a more valuable way to make graphene-doped glass highly conductive and resistant to aggressive mechanical perturbations, cracking, and oxidizing by maskless, residue-free, and free-form patterning.

We use GO as a graphene precursor to make this possible, given GO water dispersibility enabling solution processing and compatibility with large-scale fabrication techniques.^[28,29] Furthermore, we show the selective integration of the highest quality rGO into glass using LIBT and successfully apply this novel graphene–glass composite for electronics, sensing, photocatalytic, and electrothermal heating element demonstrations.

2. Results and Discussion

2.1. Laser-Induced Back-Reduction/Transfer/Integration

The concept developed in this work is summarized in **Figure 1**. The novelty and major hypothesis of our approach is the reduction of graphene oxide, graphene backward transfer, and integration into the glass substrate placed on top of GO-covered poly(ethylene terephthalate) (PET). All these processes are expected to take place with laser processing in a single step.

Laser irradiation, shining through the top glass surface, as illustrated in **Figure 1a,b**, reduces the GO film on PET and turns it into its electrically conductive rGO counterpart. Simultaneously, the rGO layers are transferred from the PET substrate up toward the glass slide on top due to the laser-induced gas release during GO reduction that generates a convection current, see **Figure 1b**.

Given the nature of this dynamic process depicted in **Figure 1b**, we hypothesize that only the lightest rGO layers would

preferentially reach the glass target. This is in contrast to the less reduced GO layers that require more kinetic energy to reach the glass. A consequence of this is that our transfer method must be intrinsically selective to the graphene-like layers with the highest quality since those are the lightest due to a lower amount of oxygen-containing groups. Besides transfer, the highly reduced GO layers could also become integrated into glass due to the high temperature, allowing the design and creation of robust glass electronics, as depicted in Figure 1c. The light-emitting diode powered through a free-form laser graphene–glass pattern in Figure 1c is an illustrative example of this.

2.2. Proof-of-Principle for Laser-Induced Graphene–Glass Composites

Raman spectroscopy is the tool of choice for the investigation of graphene materials.^[30] Thus, our single-step high-quality graphene generation and transfer hypothesis was confirmed by Raman hyperspectral imaging results in Figure 2. We analyzed an rGO-LIBT sample fabricated as described above (Note S1 and Figure S1, Supporting Information), and to our surprise, the reduction was even more drastic than we anticipated. The Raman spectra displayed the characteristic sharp peaks of graphene rather than the broad rGO peaks (see Figure 2a). As a reference for single-layer graphene, we analyzed a graphene sample obtained by chemical vapor deposition and transferred to a SiO₂/Si substrate. For the comparison, we selected the defective areas to record the spectra, as evidenced by the defect-activated D band around 1350 cm⁻¹. This spectral comparison to the graphene reference (Figure S2, Supporting Information) evidence that the characteristics of the rGO-LIBT glass-integrated layers we obtained are closer to graphene than the best laser-rGO reported until now.^[31] The Raman peak sharpness is a direct indication of the quality and crystallinity of the material including graphene. The 2D Raman band has a width of 194 and 90 cm⁻¹ for graphene oxide and chemically reduced GO.^[31] At the same time, the intensity of the 2D peak decreases with an increase in defect concentration. For rGO-LIBT, the 2D peak width of 60 cm⁻¹ (see Figure S3, Supporting Information) is comparable to that of the G peak, being even slightly sharper than the best laser-rGO reported so far with a width of 68 cm⁻¹, while the conventional thermally-reduced GO has such a negligible 2D peak that its fitting is rarely reported.^[31] Our results also contrast with the typical Raman spectra from laser-rGO.^[32]

The wrinkles and folds are typical for graphene and GO layers and are visible in the atomic force microscopy (AFM) image from rGO-LIBT in the inset of Figure 2a. These wrinkles are also evident in the original GO precursor, as shown by AFM results in Figure S4, Supporting Information. These AFM results showing the wrinkled structure characteristic of the original GO demonstrate that the final layers were transferred and integrated into the glass composite while maintaining their structural integrity.

Besides structural characteristics provided by Raman spectroscopy, the electrical conductivity also defines graphene quality. Thus, we performed electrical characterization of rGO-LIBT using current sensing AFM. These results

showed electrically conductive domains at the nanoscale (Figure S5a, Supporting Information). The excellent electrical performance of the rGO-LIBT glass nanocomposite was verified locally with current–voltage characterization showing an ohmic behavior, see Figure S5b, Supporting Information. The electrical characteristics were further confirmed using the four-probe method at the macroscale. Sheet resistance results demonstrated a low resistance of 160 Ω sq⁻¹, although with a relatively high dispersion of 40 Ω sq⁻¹, for a $\approx$ 20 μ m thickness evaluated from cross-sectional scanning electron microscopy (SEM) analysis (Figure S6, Supporting Information). These values are lower than chemical- and light-driven reduced GO reported until now with a sheet resistance at the k Ω sq⁻¹ range.^[33,34] This is a critical finding since decreasing materials resistivity is essential for electronics making laser writing electronic circuits directly into glass possible. Since the probe distance is 400 μ m, we investigated three regions of interest on the sample to collect data from the entire surface and verify the resistivity anisotropy. Calculated sheet resistance lies between 115–196 Ω sq⁻¹, while sheet resistance of ITO is 10–30 Ω sq⁻¹, and 10² to 10³ Ω sq⁻¹ are average values for thermally-annealed rGO.^[35] The *I*-*V* measurement results in Figure S7, Supporting Information, show the ohmic behavior of our material. Additionally, we investigated the influence of the number of laser pulses per point on the sheet resistance (Figure S8, Supporting Information), which shows a straightforward way to tune electrical properties (from a few Ω sq⁻¹ to tens of k Ω sq⁻¹). We hypothesize that the significant increase of sheet resistance in the 8th pulse hitting the structure is due to graphene conductive layers ablation off glass followed by the second cycle of LIBT with subsequent pulses resulting in sheet resistance drop (Figure S8, Supporting Information).

We noticed that our sample was hard to scratch, which prompted us to test the mechanical robustness. This test was done by ultrasonication of an rGO-LIBT sample for 5 min in water, which is one of the harshest cleaning methods. Remarkably, the sample remained electrically conductive, while the Raman spectra in Figure S9, Supporting Information, confirmed that graphene persisted integrated into the glass substrate after ultrasonication.

These results indicate that the graphene layers are firmly attached and integrated into the glass, forming a conductive and robust composite withstanding mechanical scratching and ultrasonication. Moreover, as discussed later, this material also has remarkable electrothermal resilience.

2.3. The Laser-Induced Processes Behind

The mechanism behind GO laser reduction involves photochemical and photothermal contributions.^[36] The degree of each contribution depends on the laser wavelength and pulse frequency.^[37] For infrared (IR) lasers, it is assumed that the photothermal contribution dominates, while for UV lasers, a photochemical contribution determines the GO reduction.^[38] We used a 436 nm laser that should involve both mechanisms. However, as soon as electron-hole photoexcitation occurs, the

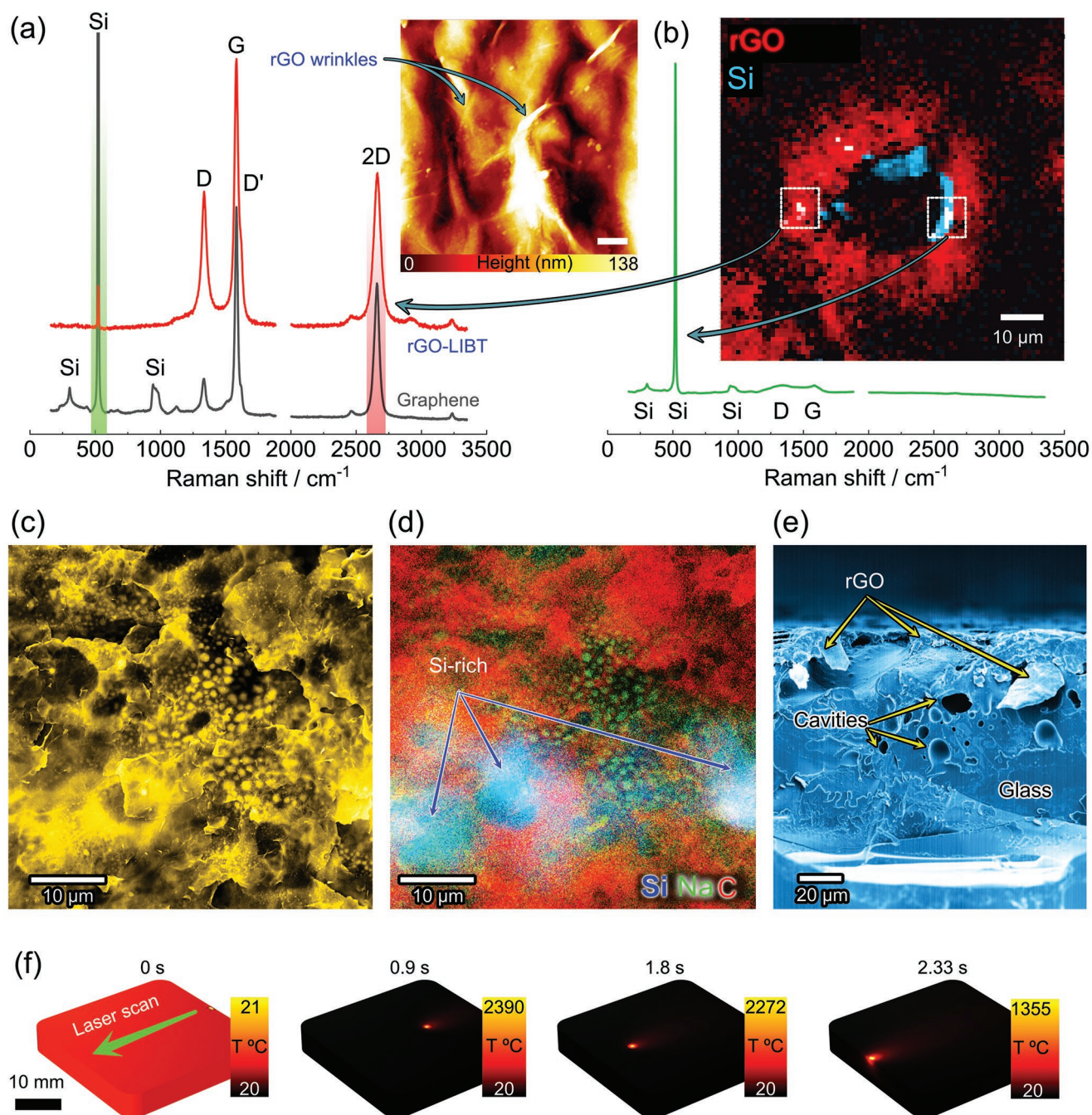


Figure 2. a) Raman spectra of the rGO-LIBT and single-layer graphene reference for sp^2 carbon (measured on folded regions). The inset shows an AFM image of the rGO-LIBT sample (scale bar is 500 nm), showing the typical wrinkles of GO. b) Hyperspectral Raman image of the sample. Red color for the 2D peak intensity of graphene and blue for the TO Si peak intensity. The sharp peaks from Si characterize the silicon region. c) SEM image. d) Elemental mapping with EDX, while all the sample is covered with carbon (red color), and with some Si and sodium-rich domains represented by blue and green colors, respectively. e) Cross-sectional imaging showing the cavities and rGO layers on the glass. f) Finite element method simulation results show the increase in temperature on the glass/GO/PET system while scanning the laser over the sample (at different times). The parameters used for the simulation were set to match our experimental conditions.

recombination of these charges is mediated by carrier-phonon scattering that increases the lattice temperature. Besides, a photochemical effect cannot explain the mass transport, the graphene integration into the glass, or even the formation of other semiconducting phases discussed below as all these

require high temperatures. Therefore, we attribute laser reduction and co-existing processes dominated by photothermal effects rather than photochemical.

The environment is another factor that influences GO reduction.^[39] Although there is no previous report on the LIBT

transfer of GO films, precedents show that a low-oxygen atmosphere increases the quality of laser-reduced GO.^[39] The spatially confined volume in our experimental configuration, in addition to high pressure and temperature, results in oxygen depletion contributing to the remarkable graphene-like characteristics of our composite.

An unexpected result from laser processing is the observation of Si in the rGO-LIBT glass (Figure 2a) and rGO/PET sides of the GO sandwich (Figure S10, Supporting Information). The Raman map in Figure 2b is color-coded so that red shows regions rich in graphene (the 2D peak intensity @2662 cm⁻¹) and blue color shows regions rich in Si (the TO mode intensity @520 cm⁻¹). Although graphene is observed everywhere in the sample, the Si peak is spatially located at the spot's edges in Figure 2b, while Raman spectra from the spots' center have no discernible features but signals at the noise level (Figure S11, Supporting Information), indicating the absence of crystalline components. As we discuss further below, the presence of spots with no crystalline material is related to hydrodynamic effects with the laser-induced forward transfer of material from glass to the PET substrate (see also Raman spectra recorded at the PET side in Figure S10, Supporting Information).

These voids, also visible in the SEM image (Figure 2c), are due to rapid heating creating a high-temperature gradient resulting in mass transfer (Benard–Marangoni convection), leaving some Si at the void edges, matching the Raman hyperspectral imaging results. Furthermore, we found that the presence of Si and sharp graphene peaks are mutually exclusive, as shown by the spectrum in Figure 2b with broad D and G peaks (see Figure S12, Supporting Information, for a zoom-in around those peaks). SEM imaging of the sample in Figure 2c evidences the sample's microstructure characterized by voids and particles. The elemental analysis mapping by EDX in Figure 2d shows that the particles in the middle of the image are rich in sodium (green color), indicating their glass composition. While most of the surface is covered by carbon (red color) and only at the top layers (Figure 2e) a few regions are rich in silicon but low in carbon, in agreement with the hyperspectral Raman imaging results. To provide further evidence on the chemical composition of our composite and indicate the changes induced by LIBT transfer, we performed an XPS analysis of the glass substrate and rGO-LIBT composite (Figure S13, Supporting Information). The results show a significant rise in the amount of carbon, precisely the number of C–C bonds (about 284.5 eV), and a change in the intensity ratios between C–C, C–O–C (≈285 eV), and O–C=O (≈288 eV), which confirm the graphene transfer to the glass surface. Furthermore, the Si 2p narrow region shows Si in the glass in two chemical states—SiO₂ (104.3) and Si–O–C/Si–O (102.5), while we see Si in our composite with a single peak of SiO₂ (103.1 eV), confirming Raman observations.

The variation in sheet resistance discussed above can be attributed to the electrically conductive graphene network disrupted by the insulating glass and semiconducting silicon domains.^[40] This explanation is supported by SEM and EDX results in Figure 2d showing the spatial distribution of such domains.

2.4. The Mechanism behind the Graphene–Glass Composite Formation

To understand our results, we must consider the dynamics of the whole laser irradiation process. The 436 nm laser does not do much to the glass slide since it is optically transparent, so the light goes through and hits the GO film on top of the PET. After the processes depicted in Figure 1b occur, the upper graphene layers on glass start absorbing light and dissipating part of the photothermal energy toward the glass. The more graphene layers attach to the glass, the more absorption and heat are generated on the glass side. At some point, the newly formed graphene–glass composite, made by incorporating graphene sheets into the melted glass, captures most of the laser light, so the mass transport process from the GO/PET target slows down. Meanwhile, pulses of light are still striking the system and are now absorbed by the graphene–glass composite so that most of the laser energy is converted into heat on the glass side resulting in silicon formation. In the end, only graphene firmly integrated into glass remains with Si-rich regions at the periphery of the laser spot and the best graphene at the outer regions of the Si domains, as shown by Raman mapping in Figure 2b. Such distribution of material along the laser spot profile could be explained by Benard–Marangoni convection, resulting in graphene transport out of the beam center due to temperature and surface tension gradients.^[41] This interpretation is supported by a high-speed recording of the LIBT process formation showing a beating behavior, see Video S1, Supporting Information. The high-speed video shows glass melting followed by melting–cooling–melting cycles giving rise to the beating. This is a result from Benard–Marangoni convection changing optical absorption during graphene–glass formation and graphene ablation, followed by another cycle of LIBT. We also observed that the graphene concentration was the lowest in periodic parts of the sample that matched the laser focus path (see Figure S14, Supporting Information). This results in graphene reduction, transfer, and integration with glass melting and Si formation. First, there is a deep SiO₂ reduction process with the emission of silanes; silanes then decompose to Si and H₂ creating a hydrogen-rich atmosphere to form new silanes under high temperature (Equation (1)),^[42] and then silicon carbide forms as evidenced by XPS results in Figure S15, Supporting Information, (Equation (2))^[43] further contributing to high-quality graphene^[44] and silicon domains (Equation (3)) formation.



Contrary to previous works that used glass or other substrates as the carrier for LIBT (the support substrate), laser integration in our case was possible only when using PET. Experimental attempts to use glass as the carrier substrate showed that although there is a backward transfer of GO, no integration to the glass substrate on top occurs. These transferred rGO layers were easily removed by dipping the sample

in an ultrasound bath for a few seconds (see Figure S16, Supporting Information). We figured out that the PET polymer is critical as the carrier substrate since, contrary to glass, PET carbonizes while heating. Although the average temperature difference by finite element method (FEM) simulation results (and temperature distribution) when using glass or PET is only 45 °C (2021 °C for glass/GO/PET and 1976 °C for glass/GO/glass), the laser-induced carbonization (only possible with PET) increases the optical absorption of the system and the photothermal transduction efficiency. We also proved that the role of GO is essential to glass integration, homogeneity, high-quality graphene formation, and electrical conductivity. This control experiment was performed by laser processing a PET/glass sandwich structure that did not contain the GO film. The results in Figure S17, Supporting Information, show that in the absence of graphene oxide, there are indeed carbon-rich deposits on the glass, but these films are poorly integrated and inhomogeneous, and Raman results show the absence of Si or graphene peaks. To sum up, lower heat dissipation and higher optical absorption after carbonization contribute to reaching higher temperatures with PET support rather than with glass. This conclusion is supported computationally by FEM simulation results of the glass/GO/PET system that show the local temperature increase above 2000 °C during laser patterning under the conditions we studied (Figure 2f and Figure S18, Supporting Information), which is much higher than the glass melting point (530–600 °C). Moreover, we hypothesized that our method should be selective to the best graphene layers integrated into the top glass substrate (the receiver). This expectation is based on the fact that the pressure released from gas formation propels rGO layers up toward the glass side during GO laser reduction. In addition, from energy conservation considerations, some photothermal and photochemical energy converts into kinetic energy, transferring graphene layers upward. Thus, this transfer process is selective to the thinnest (lightest) graphene layers that could breach the gap between the original substrate and the glass on top.

2.5. Dual-Channel Sensor and Electrothermal Heater Based on rGO-LIBT

Next, after creating the graphene–glass nanocomposite, we proceeded with their sequential functionalization with Ag nanostructures. Silver is one of the most efficient plasmonic and multifunctional materials making possible diverse applications from sensing, energy storage, or antibacterial coating for medical implants.^[45] The tuning of optical and electronic properties of the graphene–glass nanocomposite was performed using not one but two distinct ways to construct 3D Ag-based plasmonic structures to show the versatility of our material.

The first method involved the direct laser processing of a film formed by silver nanopowder (Ag NP) suspension in ethanol with poly(vinylpyrrolidone) (PVP) deposited on the top of rGO-LIBT. Laser irradiation resulted in the integration of nanoparticles into the glass-graphene composite (Note S4, Supporting Information). Although this material showed an excellent photocatalytic activity evidenced by the 4-nitrobenzenethiol

(4-NBT) to 4,4'-dimercaptoazobenzene (DMAB) conversion, this approach compromises conductivity making electrochemical detection impossible.

That is why we switched toward the Ag functionalization by electrochemical growth (Note S3, Supporting Information) from AgNO₃ aqueous solution to create the Ag-EC/rGO-LIBT microstructure shown by SEM in Figure 3b. The morphology of these structures with dendritic-shaped Ag nanostructures (Figure 3a) covering different substrate locations is encouraging since we get a high density of plasmonic hotspots critical for surface-enhanced Raman spectroscopy (SERS) applications.

The EDX mapping in Figure 3c shows that half of the sample area is richer in silicon, and the other half is richer in carbon (left and right sides, respectively). One insight from this elemental analysis map is that the regions rich in Ag must be the most electrically conductive. The region with the most extensive Ag content (right side in Figure 3c) also matches the region with the highest amount of carbon. This observation confirms our interpretation of the electrically conductive graphene network formed on glass since Ag grows exclusively on graphene. Despite the electrical connection interruptions (left half sides in Figure 3b,c), the low film resistance is compatible with the excellent graphene quality indicated by Raman spectroscopy results (Figure 2a) that point to a high concentration of delocalized π -electrons in the graphene–glass nanocomposite.

To study the sensing possibilities, we performed the electrochemical detection of 4-NBT at different concentrations using Ag-EC/rGO-LIBT as a working electrode. Figure 3d shows a representative voltammogram with the analyte concentration down to 30×10^{-9} M. The peaks at -0.86 ± 0.04 and -1.24 ± 0.04 V correspond to the 4-NBT reduction to 4-aminobenzenethiol (4-ABT).^[46]

Figure 3e demonstrates a similar level of performance in terms of sensitivity but using the optical detection of 4-NBT (LOD of 100×10^{-9} M) with SERS. Due to the plasmonically induced hot electron transfer during the Raman experiment, there is a photocatalytic conversion of 4-NBT to 4-ABT.

Such an impressive LOD is state-of-the-art for SERS substrates, which makes it promising for that particular application (see Table S1, Supporting Information). However, the literature on EC detection of 4-NBT is rather scarce; thus, a comparison with reported data eludes us at the moment. Nevertheless, these results show the multifunctionality of the same Ag/graphene/glass composite for dual-channel electrochemical and plasmonic sensing applications with sensitivities in the nanomolar range.

Until now, we have shown the sensing capabilities of our material and the possibility of driving photochemical reactions (Figure 3d,e, and Figure S19, Supporting Information). However, a heating element is indispensable for other applications including gas sensors, chemical reactors, defrost, and antifog glasses. Therefore, as a final exploration of the limits of our technology, we created and demonstrated an electrothermal heater. The results are summarized in Figure 3f showing three rGO-LIBT rectangles patterned on glass, with the one in the middle under a 12 V electrical potential showing a remarkable temperature rise above 300 °C powered by the

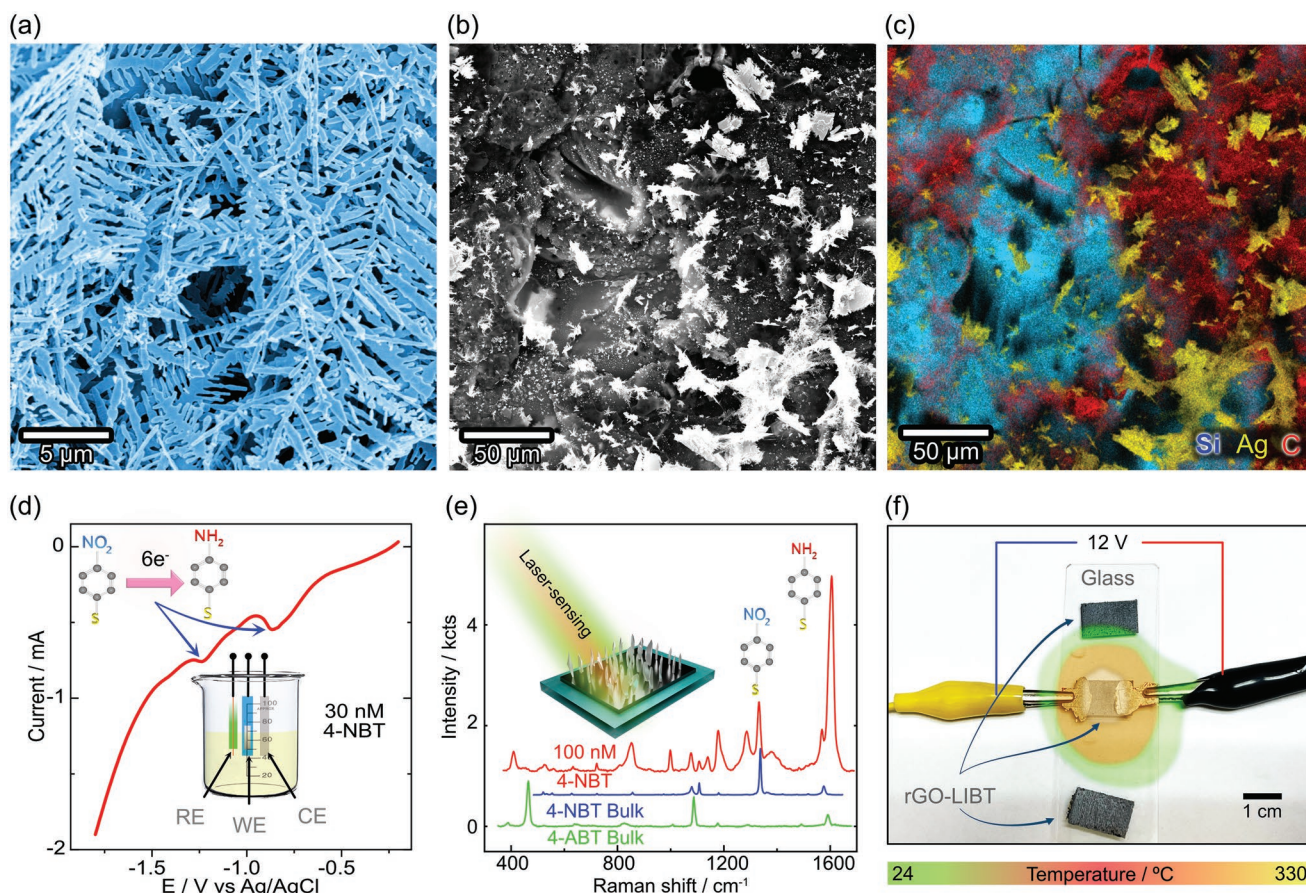


Figure 3. a) SEM image of rGO-LIBT with electrochemically formed Ag nanostructures. b) SEM image of the electrochemically deposited Ag nanostructures on the graphene–glass composite. c) Elemental mapping of the sample shows Si, Ag, and C with blue, yellow, and red colors, respectively. d) Voltammogram showing the electrochemical reduction of 4-NBT to 4-ABT, concentration 30×10^{-9} M. e) Surface-enhanced Raman spectroscopy (SERS) spectrum for 4-NBT at 100×10^{-9} M. The hot-electron transfer results in the photocatalytic reduction to 4-aminobenzenethiol (4-ABT), together with the 4-NBT and 4-ABT powder reference spectra. f) Picture of three rGO-LIBT rectangles on the glass where the middle one was powered by 12 V potential. The temperature image captured by a thermal camera overlaps with the device picture showing the heat distribution and the temperature reached.

same voltage as in car batteries. The color-coded temperature image was acquired with a thermal camera and overlapped with the device's photography showing the temperature range and spatial distribution. We also verified the stability of the device under continuous operation for 48 h at a temperature of $\approx 120^\circ\text{C}$ reached by applying 8 V. This is twice the temperature of commercial glass heating elements in cars that reach a temperature of about 60°C (see Figure S19, Supporting Information). In addition, optical imaging of rGO-LIBT films after operation at different regimes confirmed the structural stability of the material (see Figure S19, Supporting Information). These results are critical for industrial applications since the device integrated into glass survived such temperature gradients without structural damage, demonstrating excellent reliability over 48 h of continuous work.

This work has a high potential for future insights and findings. For example, there are still open questions such as the exact role of Si domains in the material's electronic properties and the possibility of exploiting these domains for energy applications. We hypothesize that convection currents and redeposition cycles are responsible for the beating behavior

observed in high-speed imaging recorded during LIBT formation (see Video S1, Supporting Information). A detailed understanding of this process involves a multiphysics approach combining hydrodynamics and electromagnetism in a spatially-confined volume that is a whole research topic on its own, and thus, well beyond the scope of this work.^[41] Nevertheless, the simple experimental configuration to create the graphene–glass nanocomposite, which has never been done before, opens the door to complex phenomena, making fertile ground for future fundamental discoveries widely available.

Besides a fundamental understanding, this exciting material and its ease of fabrication with high optical absorption, robustness, and electrical conductivity, lead us to anticipate further developments, such as free-form photovoltaic applications^[47] or new materials, for energy storage that we are now intensively investigating.

Graphene is the most studied nanomaterial to date, while glass is omnipresent in our lives. Compositing these two together in an environmentally-friendly and economically-competitive way with ultrarobustness enabling real-life applications and free-form patterning capabilities has strong technological

and fundamental implications. Moreover, our work was based on a common graphene source widely available and used by the scientific community (GO from Graphenea), and we have shown that our method produces rGO layers with the highest structural quality and the best sheet-resistance than any other laser-reduced method reported so far.

3. Conclusions and Outlook

This work presents a novel approach to firmly integrating high-quality graphene into glass using the backward transfer of laser-reduced GO from PET to glass. This results in electrically conductive ($160 \Omega \text{ sq}^{-1}$) and durable graphene–glass hybrid nanostructures for electronics that withstand mechanical scratching, ultrasonication, and elevated temperatures. We achieved the highest quality of laser-rGO to date, which allows us also to control the electrical resistance in our new nanocomposite material from a few Ω to the $\text{k}\Omega$ range. We further functionalized our conductive graphene–glass composites with Ag nanostructures to design electrochemical and plasmonic sensors, demonstrating remarkable limits of detection down to the nanomolar range. Finally, we scratched the surface of what is possible with our development showing photocatalytic applications to drive chemical transformations with light, electrothermal elements, and free-form electronic circuits to power superbright LEDs.

Adding multifunctionality to glass in an inexpensive, free-form, scalable, and environmentally friendly way opens the door to many applications. Consider such properties as tunable surface conductivity made on a transparent and universal material. Thus, our nanocomposite could find its way from TV sets and computer monitor displays to emerging applications such as smart glasses with augmented reality features and photovoltaic cells. The application of these electromechanical sensors could provide several functions in terms of safety, durability, and reliability. For example, they may be used to monitor structural integrity in buildings, cars, and planes, by measuring interruptions within their conductive path due to failure.

4. Experimental Section

Materials: GO water dispersion with a 4 mg mL^{-1} concentration was obtained from Graphenea Inc. (Cambridge, USA). The Ag NP was purchased from Advanced Powder Technologies LLC (Tomsk, Russia) and produced by the electric explosion of wire method in an argon atmosphere. The single-particle size was 80–100 nm, and the bulk density was $\approx 5.8 \text{ g cm}^{-3}$. Silver nitrate (AgNO_3) corresponded to the Russian State Standardization System No. 1277–75. 4-NBT, technical grade 80%, 4-ABT (>97%), and PVP with a number-average molecular weight (M_n) of 40 000 were obtained from Sigma-Aldrich, Russia. PET with a thickness of 0.6 mm was used as a substrate for GO deposition. $26 \times 76 \text{ mm}$ glass microscope slides with 1 mm thickness were used as target substrates. Throughout this work, deionized (DI) water, distilled water, and ethanol (EtOH , >99.5%) were used.

Thin-Film Deposition: The GO solution was used as received. Before use, it was sonicated (PS-20 Shenzhen Kejie Ultrasonic Technology Co., Ltd., ultrasonic power 120 W, 5 min) at room temperature. Then, the drop-casting technique was used to obtain a uniform distribution of GO across the PET area (1976 mm^2). As a result, the volume of GO was

$1.8 \mu\text{L}$ per unit area. Subsequently, the obtained GO film was dried at room temperature for 24 h.

Laser-Induced Backward Transfer: A sandwich PET/GO/glass structure (from bottom to top) was used to perform LIBT. To ensure close contact between the substrates, glass and PET/GO were pressed together using magnets and a metal table underneath the sandwich structure. A laser was used with a 9.4 ms pulse length, frequency of 87.7 Hz, 436 nm wavelength, and power varying from 7.8 mW in standby mode with 1423 mW at its maximum power. The laser beam spot had a rectangular shape of $316 \mu\text{m} \times 148 \mu\text{m}$ as major and minor axes and was focused on GO/PET through the top glass slide, as depicted in Figure 1a. Samples reported in the manuscript were prepared with a 1422.5 mW laser power; however, during the fabrication process optimization, a set of different parameters was tested including the number of pulses per single spot (Figure S8, Supporting Information).

The ability to form a graphene–glass composite from PET/glass without GO was investigated. Laser processing was performed with the same setup under the same conditions as with GO.

Silver Deposition: Silver nanoparticles were deposited on rGO-LIBT glass using the laser-based method (Figure S19, Supporting Information) and electrochemical reduction (Figure 3) to explore the photocatalytic properties.

Electrochemical Method: A P-45X potentiostat/galvanostat (Electrochemical Instruments, Russia) was used for the direct electrodeposition of Ag on rGO-LIBT samples from an AgNO_3 aqueous solution (0.1 M), under a constant negative potential of -3 V for 5 min. A platinum electrode was used as the counter electrode (CE) and pseudo reference electrode in one. After deposition, the AgNO_3 residues were removed with distilled water.

Optical Method: The integration of Ag NPs was also carried out by direct laser processing. Spherical AgNPs with a size of 80–100 nm were purchased from “Advanced powder technologies” (Russia) in powder form. First, 20 mg of Ag NPs were added to a 1.5 mL PVP ethanolic solution (5 mg per 1.5 mL). The mixture was sonicated at 120 W for 20 min at room temperature. Then, 150 μL of Ag NPs–PVP solution were deposited onto the rGO-LIBT glass sample by drop-casting and dried at room temperature. Then, the samples were irradiated with a laser power of 1423 mW and quickly sonicated to remove the Ag NPs that were not integrated.

Chemical Sensor: The multifunctional sensor performance was evaluated to detect 4-NBT. For this, Ag-EC/rGO-LIBT samples were soaked in a 4-NBT solution ($1 \times 10^{-3} \text{ M}$) for 10 h in the dark, followed by cleaning with EtOH and distilled water.

SEM and EDX: TESCAN MIRA3 SEM with an LMU chamber (Tescan Orsay Holding, a.s., Czech Republic) and an energy dispersive microanalysis system AztecLive Advanced Ultim Max 40 with a nitrogen-free detector (Oxford Instruments Analytical Ltd., England) was used for morphological and elemental characterization of the samples.

Raman Spectroscopy: Raman measurements were carried out using a confocal Raman microscope (NTEGRA Spectra, NT-MDT, Russia). The Raman microscope was configured with a 633 nm diode laser. The laser beam was focused on the rGO-LIBT sample using a 100 $\times$ Mitutoyo objective with a 0.7 numerical aperture. Signal was collected by an electron-multiplying charge-coupled detector (EMCCD) (Andor Newton, UK) cooled to -65°C . Raman mapping was used to visualize the distribution of 4-NBT on Ag-LIC/rGO-LIBT with SERS. The acquisition time ranged from 0.1 to 0.5 s per pixel, at an image pixel resolution between 1 and 5 μm . SERS sensing measurements on AgEC/rGO-LIBT were performed using a 20 $\times$ magnification objective and 532 nm laser diode. LOD was experimentally defined by decreasing concentration until there were no visible peaks of the target analyte.

Atomic Force Microscopy: The surface morphology of rGO-LIBT glass samples was investigated using NTEGRA atomic force microscope (NT-MDT, Russia). The AFM images were obtained by scanning the sample's surface with a conventional silicon cantilever.

Sheet Resistance: MST 4000A microprobe station (MS Tech Korea Co Ltd, South Korea) was used to position the tips in a square configuration

at a distance of 400 μm between each on the $1 \times 1 \text{ cm}^2$ sample. Electrical characterization was performed on the potentiostat-galvanostat P-45X (Electrochemical instruments, Russia). Sheet resistance was calculated using Equation (4):^[48]

$$R_{\text{sheet}} = \frac{2\pi V}{\ln 2 I} \quad (4)$$

where V [V] is the voltage drop between two probes in the top corners of the square, and I [A] is the current injected by two probes at the bottom of the square.

Electrochemical Characterization: Potentiostat/galvanostat P-45X with impedance modulus FRA-24 M (Electrochemical instruments, Russia) was used to perform electrochemical characterization and sensing. A standard three-electrode cell was assembled with the spiral Pt, Ag/AgCl, and rGO-LIBT as counter, reference, and working electrodes. 4-NBT sensing was done in an aqueous solution with KOH (0.1 M) as a supporting electrolyte. LOD was experimentally defined by decreasing concentration until there were no visible peaks from the targeted analyte.

FEM Modeling: Laser heating simulation was performed in commercial software COMSOL Multiphysics using the Time-Dependent Heat Transfer in Solids module. Laser heating was modeled as a heat load on the surface over time. The sample consisted of three layers from bottom to top: PET with 0.6 mm thickness, GO with 6 μm thickness, and glass with 1 mm thickness. Sample width and depth had sizes of 10 mm. Laser power was set at 1423 mW. The laser pulse width was set at 9.4 ms with a period of 11.4 ms; the laser spot diameter was measured and set at 148 μm . The heating time was set as 2330 ms according to the experimental measurements.

High-speed video recording was performed in a single spot by the high-speed imaging system (CuBr vapor brightness amplifier).

Electrothermal Heater: Electrothermal transduction was carried out by applying a constant voltage by a DC power supply through a LIBT sample ($15 \times 10 \text{ mm}^2$) with contacts made with silver paint.

Statistical Analysis: The sheet resistance variations across the rGO-LIBT glass nanocomposite samples were evaluated. A total of three points per sample were measured. 1000 voltage data points (at constant current) were recorded at every spot for each sample. Sheet resistance values were calculated from Equation (4) and averaged to elucidate the influence of noise and instrumental error. The final sheet resistance values for each sample were calculated by averaging the values recorded from three different points per sample.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

R.D.R.: Conceptualization, methodology, investigation, visualization, and writing—original draft. M.F.: Methodology, investigation, formal analysis, and writing—original draft. A.G.: Methodology, investigation, formal analysis, and writing—original draft. S.S.: Methodology, investigation, formal analysis, and writing—original draft. I.P.: Investigation and visualization. L.L.: Formal analysis and writing—review and editing. A.A.: Methodology and software. A.L.: Formal analysis and writing—review and editing. R.W.: Formal analysis and writing—review and editing. J.S.: Investigation and writing—review & editing. Q.L.: Formal analysis and writing—review and editing. X.J.: Formal analysis and writing—review and editing. C.C.: Formal analysis and writing—review and editing. O.K.: Formal analysis, writing—review and editing, and funding acquisition. E.S.: Conceptualization, funding acquisition, and writing—review and editing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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conductive nanostructures, glass electronics, graphene heaters, graphene oxide, laser-engineered nanostructures, laser-induced backward transfer, sensors

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