

Enhancement of Electrical Conductivity of Graphene-Coated Glass Slides via Sulfuric Acid Chemical Passivation: A Systematic Study using the Four-Point Probe Method



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ABSTRACT

Graphene oxide (GO) is a promising material for electrochemical applications due to its high surface area and functional tunability. However, its inherent electrical resistance—caused by abundant oxygen-containing groups—limits its use in high-performance energy devices. Enhancing its conductivity is essential to unlock its full potential, especially in supercapacitor electrodes. This study demonstrates that sulfuric acid chemical passivation significantly enhances the electrical conductivity of graphene-coated glass slides, with the optimal effect observed at a concentration of 0.6 M. At this concentration, the samples exhibit the lowest resistivity and stable thickness, indicating improved uniformity and minimal structural degradation. However, higher concentrations (0.7 M–0.9 M) lead to over-passivation, causing a decline in conductivity and signs of material degradation. These findings highlight 0.6 M H₂SO₄ as the most effective concentration for boosting graphene's conductive properties through a simple and scalable post-treatment process. This report delves into the fundamental properties of graphene, the methodology of the four-point probe method for characterization, the underlying mechanisms of sulfuric acid passivation, and recent breakthroughs in scalable graphene production and post-treatment techniques, including key materials and challenges.

Keywords:

Energy storage,
Four-point Probe,
Graphene,
Supercapacitors.

INTRODUCTION

Graphene, a single-layer carbon allotrope arranged in a hexagonal honeycomb lattice, stands as the prototypical two-dimensional (2D) material, with a theoretical thickness of ~0.345 nm (Geim, 2009). Its exceptional electrical conductivity, reaching up to ~100 MS/m—significantly higher than that of copper (~59 MS/m)—positions it as a superior conductor at the nanoscale (Köhne & Rizzi, 2021). Graphene also exhibits thermal conductivities of 4,840–5,300 W·m⁻¹·K⁻¹ for suspended monolayers—far beyond that of most metals—making it highly promising for thermal management applications (Balandin et al., 2008). Moreover, its mechanical strength (Young's modulus ~1 TPa) and transparency (absorbing only ~2.3% of incident light) enable a unique combination of flexibility, durability, and optical clarity (Geim, 2009). From an electronic perspective, pristine graphene behaves as a zero-bandgap semimetal, exhibiting exceptionally high charge-carrier mobility, with up to 200,000 cm²/V·s observed in suspended samples and ~40,000 cm²/V·s on SiO₂ substrates—outperforming conventional

semiconductors by several orders of magnitude (Novoselov et al., 2005; Chen et al., 2008).

At the charge neutrality point, a monolayer typically exhibits sheet resistance around 6 kΩ/□ (Morozov et al., 2008).

Graphene is produced via various methods—including mechanical exfoliation, liquid-phase exfoliation, silicon carbide sublimation, and chemical vapor deposition (CVD)—with CVD offering the most promise for scalable, high-quality, and large-area films (Geim, 2009; Köhne & Rizzi, 2021).

These exceptional electrical, thermal, mechanical, and optical properties render graphene a transformative material across fields such as flexible electronics, optoelectronics (touchscreens, OLEDs), energy storage (batteries, supercapacitors), composites, aerospace, and bio-sensing, where it enables devices that are lighter, stronger, more efficient, and resistant to environmental stressors (Balandin et al., 2008; Köhne & Rizzi, 2021).

The fundamental principle of the 4pp system involves four equally spaced, collinear probes that establish electrical contact with the material under test.10 A direct

current (I) is precisely applied through the two outer probes, inducing a voltage drop across the material. Simultaneously, the voltage difference (ΔV) is measured across the two inner probes. (Saini et al., 2024; Ossila, n.d.). The sheet resistance (R_s) is then calculated using the formula:

$$R_s = (\pi / \ln(2)) \times (\Delta V / I) \quad (1)$$

A significant advantage of the 4pp method is its inherent ability to eliminate the effects of contact resistance. This is crucial for accurate measurements on thin conductive layers, where the resistance at the interface between the probe and the material can otherwise introduce substantial errors and significantly impact the results.

In this study we will be using the 4pp method to study the electrical properties and enhancement of conductivity of chemically passivated Graphene Oxide deposited on glass slides.

A fixed volume of 100 μL per drop was dispensed onto each slide using a micropipette. Slides were left to air dry under a dust-free cover to form uniform GO coatings.

GO-coated slides were immersed in 50 mL of sulfuric acid solutions of varying concentrations (0.1 M to 0.9 M), each for 10 minutes at room temperature. Slides were thoroughly rinsed with DI water to remove excess acid. Samples were dried at 60 $^{\circ}\text{C}$ for 1 hour.

Each GO-coated glass slide was labeled clearly according to its treatment. Ensuring the sample surface was clean and dry. The thickness of the film was measured and recorded using a surface profiler. The four-point probe and source meter was turned on and the probe head gently lowered onto the sample surface using the micrometer-controlled vertical stage to ensure all four tips make uniform contact. Sheet resistance and resistivity measurements were all made at room temperature.

MATERIALS AND METHODS

Experimental Method

Standard microscope glass slides (25 mm $\times$ 75 mm) were cleaned using isopropanol and DI water, then dried. 0.5 g of GO was dispersed in 20 mL of DI water to form a uniform slurry.

RESULTS AND DISCUSSION

This section presents the results following the chemical passivation process, the electrical properties of the GO-coated glass which includes the sheet resistance and resistivity of the samples.

Table 1: Four Point Probe Results for 0.1M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	108.2	0.0426	21.85	3.9
2.500	0.000	107.9	0.0424	21.90	3.9
0.000	2.500	108.1	0.0425	21.87	3.9
-2.500	0.000	107.8	0.0424	21.90	3.9
0.000	-2.500	108.3	0.0426	21.85	3.9

Table 2: Four Point Probe Results for 0.2M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	106.3	0.0419	22.11	3.9
2.500	0.000	105.8	0.0417	22.16	3.9
0.000	2.500	106.1	0.0418	22.13	3.9
-2.500	0.000	106.2	0.0418	22.13	3.9
0.000	-2.500	106.0	0.0418	22.13	3.9

Table 3: Four Point Probe Results for 0.3M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	104.2	0.0411	22.46	3.9
2.500	0.000	104.0	0.0410	22.50	3.9
0.000	2.500	103.9	0.0409	22.54	3.9
-2.500	0.000	104.1	0.0410	22.50	3.9
0.000	-2.500	104.0	0.0410	22.50	3.9

Table 4: Four Point Probe Results for 0.4M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	102.6	0.0401	22.72	3.9
2.500	0.000	102.4	0.0400	22.75	3.9
0.000	2.500	102.5	0.0400	22.75	3.9
-2.500	0.000	102.3	0.0399	22.78	3.9
0.000	-2.500	102.5	0.0400	22.75	3.9

Table 5: Four Point Probe Results For 0.5M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	101.63	0.0396	22.43	3.9
2.500	0.000	101.52	0.0395	22.44	3.9
0.000	2.500	101.78	0.0396	22.46	3.9
-2.500	0.000	101.63	0.0396	22.43	3.9
0.000	-2.500	101.31	0.0395	22.41	3.9

Table 6: Four Point Probe Results for 0.6M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	100.6	0.0392	22.72	3.9
2.500	0.000	100.4	0.0391	22.76	3.9
0.000	2.500	100.5	0.0392	22.72	3.9
-2.500	0.000	100.3	0.0391	22.76	3.9
0.000	-2.500	100.7	0.0392	22.72	3.9

Table 7: Four Point Probe Results for 0.7M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	101.1	0.0402	22.33	3.7
2.500	0.000	101.3	0.0403	22.31	3.7
0.000	2.500	101.0	0.0401	22.35	3.7
-2.500	0.000	101.2	0.0402	22.33	3.7
0.000	-2.500	101.4	0.0404	22.30	3.7

Table 8: Four Point Probe Results for 0.8M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	102.0	0.0414	22.03	3.6
2.500	0.000	101.8	0.0413	22.05	3.6
0.000	2.500	102.2	0.0415	22.00	3.6
-2.500	0.000	102.0	0.0414	22.03	3.6
0.000	-2.500	102.1	0.0414	22.03	3.6

Table 9: Four Point Probe Results for 0.9M H₂SO₄ Passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	103.2	0.0432	21.63	3.5
2.500	0.000	103.0	0.0431	21.63	3.5
0.000	2.500	103.1	0.0431	21.63	3.5
-2.500	0.000	103.3	0.0433	21.57	3.5
0.000	-2.500	103.2	0.0432	21.60	3.5

Table 10: Four Point Probe Results for Reference non-passivated G.O Coated Glass Slide

X (mm)	Y (mm)	R (Ω)	Resistivity ($\Omega \cdot \text{cm}$)	Surface Conductivity (S/cm ²)	Thickness (μm)
0.000	0.000	238.60	0.0954	23.85	4.0
2.500	0.000	238.35	0.0953	23.83	4.0
0.000	2.500	238.61	0.0954	23.85	4.0
-2.500	0.000	238.47	0.0953	23.83	4.0
0.000	-2.500	239.12	0.0956	23.90	4.0

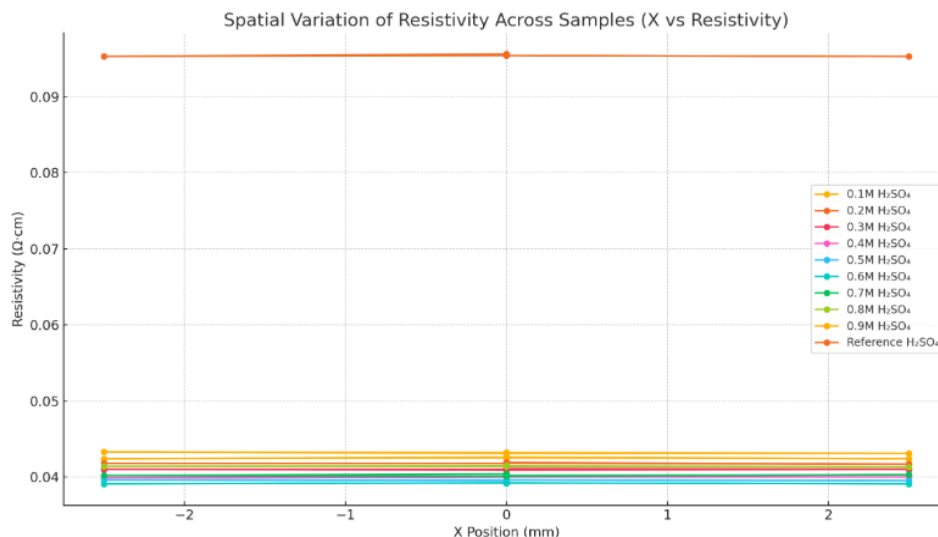


Figure 1: Combined graph for four point probe results of how resistivity changes across the X positions for each sample

The above graph shows the untreated graphene oxide sample (reference) exhibited the highest resistivity, indicating minimal electrical conductivity, a result consistent with its high content of oxygen-containing functional groups that disrupt the sp^2 carbon network and hinder electron mobility (Dreyer et al., 2010). Upon chemical passivation with sulfuric acid, a notable reduction in resistivity was observed, with the sample treated at 0.6 M H_2SO_4 showing the lowest resistivity, signifying peak conductivity enhancement.

This enhanced performance is likely due to the partial removal or rearrangement of oxygen functional groups, which restores some degree of conjugation in the carbon lattice, facilitating improved charge transport (Zhou et al., 2023). Samples treated with lower concentrations (0.1–0.5 M) showed a gradual improvement in conductivity, suggesting progressive structural modification. However, as the acid concentration increased beyond 0.6 M, a reversal trend emerged, with resistivity rising again in the 0.7–0.9 M range.

This behavior can be attributed to over-passivation or potential oxidative damage to the graphene structure, leading to partial degradation or over-functionalization, as observed in previous studies where excessive acid treatment introduced defects and disrupted conductivity pathways (Park & Ryu, 2021).

The observed improvement in conductivity with optimal H_2SO_4 passivation parallels findings by Ngari et al. (2022), who reported that introducing dopants such as lead into the graphene lattice enhanced charge transport and overall conductivity in Pb-doped rGO composites. This reinforces the idea that both chemical doping and post-synthesis surface modification are viable routes for improving the electrochemical functionality of GO-based films.

These findings strongly support the concept of an optimal passivation threshold, beyond which further chemical treatment results in diminishing returns or even adverse effects on the material's electrical performance. In this context, 0.6 M H_2SO_4 emerges as the most effective concentration for enhancing the conductivity of graphene oxide through controlled chemical passivation.

CONCLUSION

The electrical behavior of the GO films was evaluated by measuring sheet resistance and resistivity using the four-point probe method. The reference sample (untreated GO) had the highest resistivity (lowest conductivity), consistent with its high concentration of insulating oxygen groups. Samples treated with 0.1–0.5 M H_2SO_4 showed a gradual decrease in resistivity, with maximum conductivity achieved at 0.6 M, where the resistivity reached its lowest value. This improvement is attributed to the partial removal and rearrangement of functional groups, which restores electron pathways in the GO lattice. For concentrations beyond 0.6 M, a reversal trend was observed. Resistivity began to increase at 0.7 M to 0.9 M, likely due to over-passivation, excessive etching, or degradation of carbon domains — a behavior reported in literature for over-treated carbon nanomaterials. This study demonstrates that chemical passivation using sulfuric acid is a simple yet effective post-synthesis treatment to significantly improve the electrical properties of Graphene Oxide to make it more suitable for supercapacitor and energy storage applications. Future fabrication of GO-based electrodes should adopt 0.6 M H_2SO_4 as the optimal passivation concentration, as it delivered the lowest resistivity and hence best conductivity without compromising film integrity. Concentrations above 0.6 M are discouraged due to

observed structural degradation and diminishing conductivity returns, likely resulting from over-functionalization. To improve environmental sustainability, future work could explore green or low-toxicity passivation agents (e.g., citric acid, ascorbic acid) to reduce environmental and handling risks while maintaining or improving conductivity. Studies have shown that some organic acids can selectively remove oxygen functional groups and restore sp^2 hybridization.

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