

Short Communication

## Stability of Graphene/ Ultrathin $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Heterostructure under Water Impact

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We fabricate monolayer graphene coated ultrathin  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  heterostructures and perform the transport measurements to investigate the electrical stabilities of the heterostructures with integrated and hole existed graphene coatings respectively in the presence of water. Both of the samples demonstrate robust superconductivities although small degradation is observed in the latter. Graphene not only serves as an impermeable barrier but also inhibits the transverse penetration of water and loss of oxygen through the interface of the van der Waals heterostructure. Our results contribute to the promising applications of graphene as the conductive, conformal, and impermeable surface coating material on the chemically active two-dimensional crystals.

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**Keywords:** Ultrathin Bi2212, Van der Waals heterostructure, Hole, Graphene

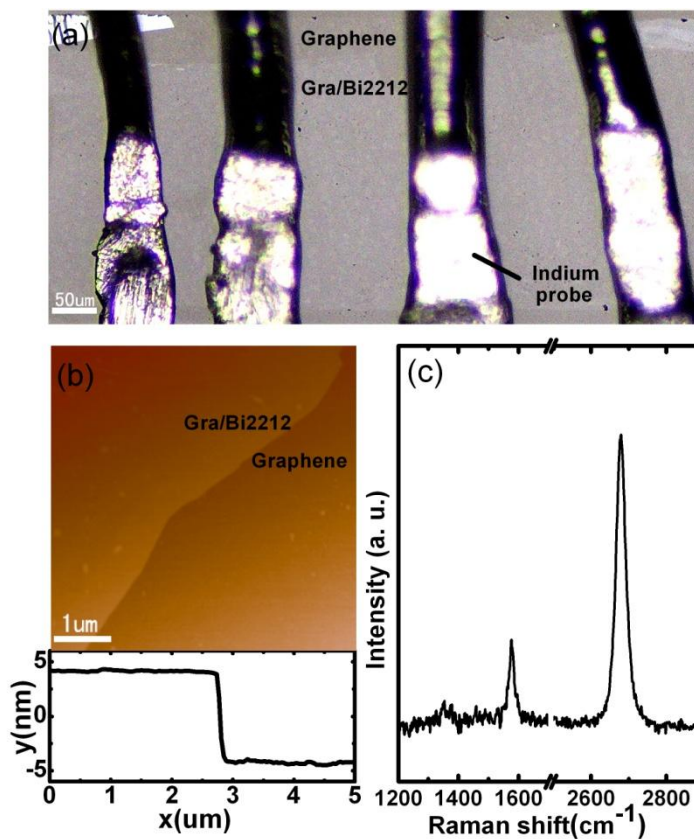
### 1. INTRODUCTION

The applications of promising two-dimensional (2D) atomic crystals are limited if they are not stable or cannot maintain the high qualities at room temperature and in air when pulled out from bulk crystals[1,2]. A typical example is that the ultrathin  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi2212) is easily deteriorated when exfoliated to atomic scale from its bulk crystal[1], which could be water-decomposed and lose oxygen in ambient conditions[3-5]. Graphene is thus introduced to present a conformal coating and is critical in maintaining the superconductivity of ultrathin Bi2212[6]. However, small holes are possible to form from transferring the chemical vapour deposition (CVD) grown graphene[7] and from artificially fabricating the van der Waals heterostructures. Whether the holes could deteriorate the

macroscopic properties is worth to investigate. Ultrathin Bi2212 presents an unparalleled sensitivity in testing the corrosion inhibiting ability of graphene. Here we report the electrical stabilities of integrated and defective graphene coated Bi2212 (Gra/Bi2212) heterostructure through water impact measurements.

## 2. EXPERIMENTAL

Continuous monolayer graphene films were synthesized by CVD on Copper foil[7]. A thin poly-methyl methacrylate (PMMA) was coated on the graphene/Cu substrate and a piece of tape was used to cover it. After the underlying Cu foil was dissolved in ammonium persulphate, the graphene film was transferred onto mechanically exfoliated thin Bi2212 flakes. PMMA and tape were removed with acetone. Contamination can clean itself off the interfaces of heterostructure[8-10]. Ultrathin Bi2212 was selected using optical microscope and atomic force microscope (AFM). The Gra/Bi2212 heterostructure (on a SiO<sub>2</sub>/Si substrate) was sized as 300×700 microns in optical microscope image (Fig. 1a).



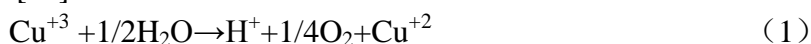
**Figure 1.** Gra/Bi2212 heterostructure. (a) Optical microscope image and (b) Atomic force microscope image of graphene coated ultrathin Bi2212 heterostructure. The AFM step is ~8.3nm, indicating the thickness of Bi2212 is about two unit cells[6,11,12]. (c) Raman spectrum of graphene films.

AFM was used to characterize the number of Bi2212 layers in the Gra/Bi2212 heterostructure. As it is shown in Fig. 1b, the AFM observation of the 8.3nm step indicates Bi2212 is around two unit cells thick, since the measured thickness is always larger than the theoretical value due to the spacing among graphene, Bi2212 and SiO<sub>2</sub>[6,11] and the chemical and van der Waals contrasts[12]. In Fig. 1c, the Raman spectrum (514nm wavelength) of graphene films on Copper foil shows a negligible D peak, indicating the defect density in our sample is very low. The displayed G (~1580cm<sup>-1</sup>), 2D Peak (~2680cm<sup>-1</sup>) and a small ratio of G/2D peak intensity ( $I_G/I_{2D} \approx 0.31$ ) are typical for single layer graphene, which was consistent with the previous report on determining the unique structure of graphene[13]. In order to detect the changes in electrical properties, transport measurements with four indium probe contacts tapped on top of the Gra/Bi2212 heterostructure were applied (Fig. 1a). As a comparison to the samples stored in ambient air, water treatment was performed. 1μl deionized liquid water was deposited on the sample with wetting area covering the graphene surface on ultrathin Bi2212. The water treated samples were measured after stored in thermostat for one day at room temperature.

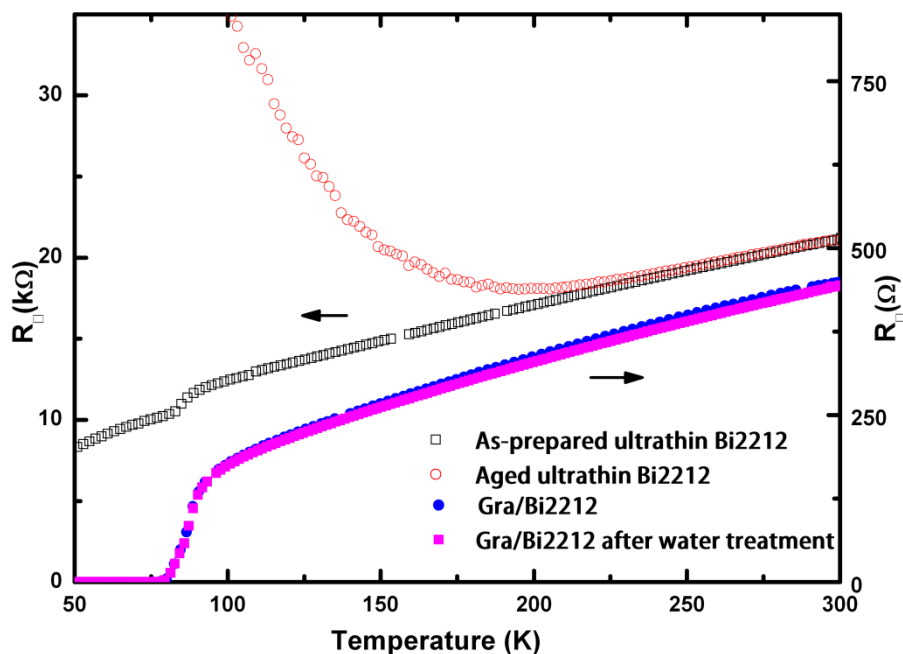
### 3. RESULT AND DISCUSSION

Integrated graphene coatings could help protect the electrical properties in the underneath ultrathin Bi2212. Since the discovery of high transition temperature cuprate superconductors, continuous efforts were focused on turning their susceptibility to chemical attacks[14-16]. In Fig. 2 (left axis) we compared two *R-T* curves of the same Bi2212 ultrathin layer, one measured immediately after mechanical exfoliation and the other measured an hour later, just after the first measurement while still keeping the sample in vacuum. Both of them showed no distinguished superconductivities though similarly they first demonstrated the linearly cooling resistances, whose origins for their consistencies in the non-superconducting samples were not understood. Remarkable degradation was observed in the second measurement as its resistivity turned upward at low temperatures.

The deterioration of Bi2212 ultrathin layer might be due to the decomposition induced by water vapour when transferring the sample in air and by loss of oxygen. Water was considered as the dominate cause to the deterioration of superconductivity in the water treated bulk crystal. At room temperature, quick redox reactions with water could deteriorate the superconductivity of bulk cuprate superconductors by producing nonsuperconducting phases[17]. Rosamilia *et al.* showed the reaction[18]:



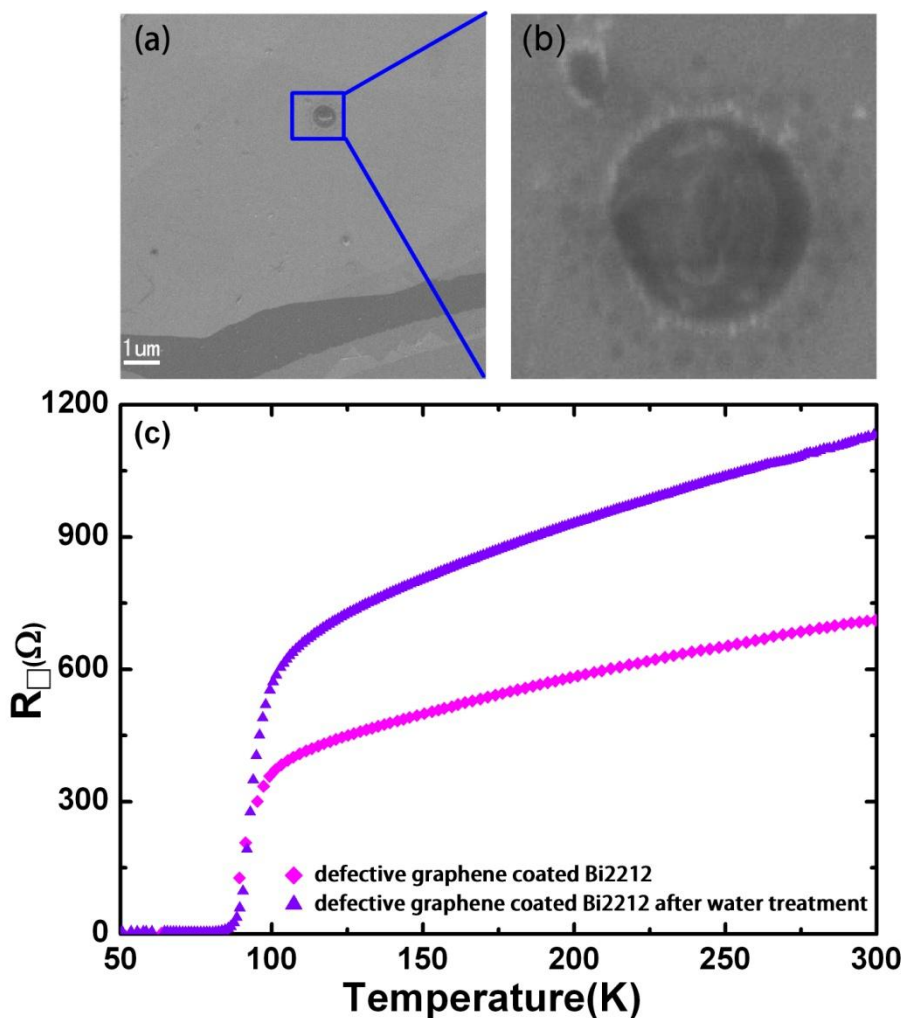
Non superconducting Bi<sub>2</sub>CuO<sub>4</sub>, SrCO<sub>3</sub>, CaCO<sub>3</sub>, and CuO were discovered as the resultant end products of the Bi2212 water reaction[3]. Besides, partial loss of oxygen in the topmost layer of Bi2212 crystal could also decrease the superconductivity[4,5]. However, the bare Bi2212, when exfoliated to 2D atomic layer, is entirely insulating even in oxygen annealed atmosphere[1,2]. Graphene is thus introduced to protect the underneath ultrathin Bi2212, which is observed to be effective in air[6]. As a comparison water treatment was performed to observe the electrical properties under water impact.



**Figure 2.** Electrical stability in integrated graphene coated Bi2212 heterostructure.  $R$ - $T$  curves for uncoated ultrathin Bi2212 (hollow labels in left axis) and Gra/Bi2212 heterostructure (solid labels in right axis) under impact of water. Superconductivities are deteriorated for uncoated ultrathin Bi2212 and nearly unchanged for the latter after water treatment.

It is intriguing to find the monolayer graphene could defend against macroscopic amount of liquid water. As shown in Fig. 2 (right axis), superconductivities and even the whole electrical properties in the water treated heterostructure are preserved as same as in the water isolated one. In the Gra/Bi2212 heterostructure, the inert graphene coating stands as a stable barrier to the ionic reaction whether caused by liquid water or losing oxygen.

After observing the stable electrical properties in heterostructures with the integrated graphene coating, we now turn our attention to the samples with defective graphene. Defects like vacancies and dislocations, introduced by synthesizing and transferring, are widely observed[19-21]. Despite the defects are varied in size and type, it is valuable to investigate the small holes which are formed spontaneously during synthesizing graphene and fabricating the devices. In statics of our samples, superconductivities are observed in heterostructures where the diameters of holes in the graphene coating are within 2  $\mu\text{m}$ . In these defective graphene coated samples where superconductivities do not get vanished facing water vapour in ambient air, we investigate the extreme conditions of water impacts by dropping liquid water to the surface of the hole existed sample. As it was shown in the blue frame in Fig. 3(a), a surface hole with a diameter within 1-micron was observed in the graphene coating by the scanning electron microscope (SEM). Fig. 3(b) was a magnified SEM image of the surface hole. Four probe transport measurements with the surface hole sited between the two voltage electrodes were performed. The defective sample clearly demonstrated the presence of superconductivity following the linearly cooling resistivity (Fig. 3(c)). The bare ultrathin Bi2212, where was in the defective area and exposed to air, should be destroyed and nearly lose conductivity. The stability of electrical properties was due to transports through other areas with graphene coating.



**Figure 3.** Defective graphene coated Bi2212 heterostructure. (a) Scanning electron microscope of defective graphene coated Bi2212 heterostructure and (b) a magnified image of the surface hole. The surface hole (with a diameter less than 1μm) in graphene coating is defected spontaneously due to synthesizing graphene and fabricating the heterostructure. (c)  $R-T$  curves for the heterostructure with defective graphene coating. Superconductivity is still preserved in the water treated sample.

Take a further investigation into the inhibition to the transverse deterioration, water treatment was applied to the hole existed sample. It was found that after treated with macroscopic liquid water, the hole existed Gra/Bi2212 heterostructure only showed less than a half increase of resistivity at normal state but demonstrated nearly no decrease of transition temperature, as it was seen in Fig. 3(c). The fact indicates that not all the underneath layer is deteriorated in the presence of water even if the graphene coating is defected with the observed holes. Though the explanation for the degradation is not clear, the demonstrated superconductivity implies limited or no water was penetrated through the interface of the Gra/Bi2212 heterostructure. The defective graphene can still inhibit the transverse penetration of water reaction and loss of oxygen. The van der Waals heterostructure is more than just a mechanical stack of multilayers but can provide strength to inhibit transverse corrosion to the underneath layer.

#### 4. CONCLUSION

In conclusion, graphene is leading an unequivocal advantage as a surface material in protecting the electrical properties in the Gra/Bi2212 heterostructure. When coated with monolayer graphene, the previous easily decomposed ultrathin Bi2212 is able to get stable electrical properties in the presence of liquid water. Even with the coating of graphene with holes due to synthesization and fabrication, the sample still demonstrates robust superconductivity in air and in aqueous conditions. Graphene not only serves as an impermeable barrier but also inhibits the transverse penetration of water and loss of oxygen through the interface of the van der Waals heterostructure. These preliminary, yet reproducible observations imply a vast of promising applications in utilizing graphene as a surface coating material.

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#### Author contributions

T.H. planned the research. Y.L., L.C. and M.W. performed the measurements. D.J. and X.Z. fabricated the sample. T.H., D.J., Y.L., X.L., and Y.S. discussed the results. Y.L., D.J. and T.H. wrote the paper.

#### Author Information

The authors declare no competing financial interests.

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