Supporting Information

Probing Graphene Edges *via* Raman Scattering

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After the preparation of this manuscript, we became aware of a similar manuscript on graphene edges from L. G. Cançado *et al*. This paper can be accessed from e-print services (http://lanl.arxiv.org/PS_cache/arxiv/pdf/0802/0802.3709v1.pdf). The authors measured the spatial dependence of the D band to be ~ 40 nm, which is in good agreement with our upper bound (~ 70 nm) determined in this work. Here, we present a detailed comparison of these two papers to justify our results as well as our choice of model for the D-band scattering from edges.

The authors of the arXiv paper analyze the D-band intensity by addressing scattering in terms of the material-specific Raman susceptibility χ_s. This term is then related to the experimentally measured line scan profile by means of a convolution of this susceptibility (which contains a spatial dependence on the edge) and the incident laser intensity (Eq. 1 in the arXiv paper). Given the well-behaved nature of the Raman susceptibility functions chosen by the authors, this procedure is in essence identical to the definition of Raman scattering efficiency functions in our paper, the differences here existing only in the choice of model for the scattering efficiency. A detailed comparison between the two papers reveals a number of differences between the two papers.

Comparison of laser beam waist:

Firstly, the arXiv paper uses a confocal line scan of fluorescence from a single Nile Blue molecule to determine the properties of the incident gaussian laser beam through a N.A. 1.4 lens, obtaining a beam waist of 186.5 nm. Our paper determines both beam waist and graphene edge position simultaneously via the line scan of the G-band. While not shown in our paper, a numerical calculation of the effect of the uneven edge on the calculated beam waist revealed the 3-nm edge variation to have no effect on the measured waist. The waist we obtained using a N.A. 0.94 lens was 400 ± 50 nm, which is in excellent agreement with the 400-nm spot size reported by the manufacturers of our microRaman system (Renishaw, Inc.).

Comparison between models:

Secondly, the authors of the arXiv paper showed that the G-band scattering efficiency is well-described by a step function positioned at the edge, an assumption we made in our determination of the beam waist. For their fit of the D band scattering, they proceeded to choose a model exhibiting exponential decay from the edge, with some decay constant χ_D that they used in their evaluation of the phase-breaking length. In comparison, our paper modeled the scattering efficiency by a sum of step functions, creating a "boxcar" of width Δ over which the scattering was confined. We did in fact try a fitting function of the type described in the arXiv paper, we obtained a value for χ_D similar to that obtained by the authors of that work. However, the corresponding uncertainty (obtained from the error matrix of the least-squares analysis) was similar to that of the boxcar fit function, and as the figure shows, the fact that a minimum exists for the least-squares analysis does not mean that it is particularly meaningful. Comparison of the resulting convolutions of the two fitting functions (Fig. S1) shows no real benefit to using one fitting function over the other, in terms of obtainable values for the width.

Comparison between the experimental value:

Finally, the arXiv paper reports a value for χ_D that they obtain via a least-squares fitting of their model. However, they (a) appear to have obtained this value by analyzing the line scan of a single graphene edge, and (b) provide nothing in the way of error analysis. By contrast, we performed a rigorous error matrix analysis of our fit, looking at 10 different edges on 5 different graphene flakes, incorporating the uncertainty involved in the beam parameters and edge location in our determination of δ and its uncertainty. We find the best fit for δ from the least squares analysis to be 0.003 nm, with an uncertainty (that is limited by whatever instrumental errors may exist in the actual data) obtained by the error matrix analysis of 36 nm. We are not claiming that the scattering takes place over a boxcar function of width 70 nm; rather, we claim that the scattering is confined to a region *at most* 70 nm in width, but in all likelihood smaller than this.

A brief word about signal to noise ratios – the S/N of our line scans is not as high as one might wish (or as obtained in the arXiv paper). First, we wish to point out that we minimized both the incident laser flux and time of exposure to avoid photoreaction of the reactive graphene edge in air. Our low S/N ratio does not limit the validity of the error matrix analysis that we performed – it merely increases the uncertainty one obtains for a given variable. That the S/N was not ideal no doubt corresponds to the uncertainty obtained for δ – however, improvement of the S/N ratio would only lead to a reduction in the uncertainty, strengthening the position that the scattering is confined to the edge.

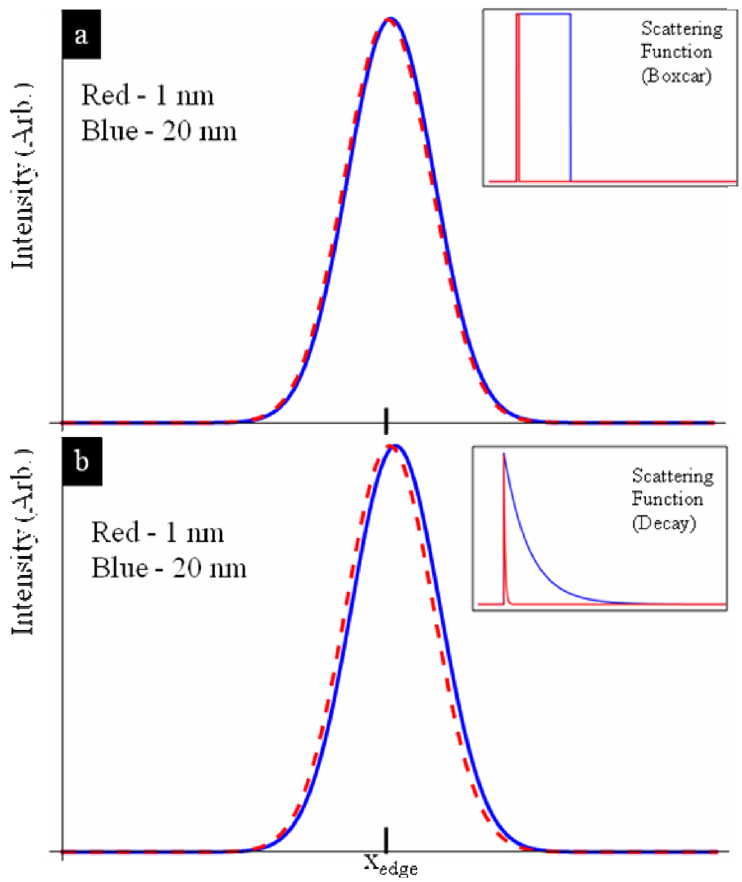

Figure S1: (a) Using the boxcar fit function for the Raman scattering efficiency (this work), we show the convoluted D band intensity for width values of 1 nm (red) and 20 nm (blue), as shown in the inset. The two curves almost overlap; there is a small offset in the position which when corrected for reveals a near-perfect overlap. Increasing the width to ~50 nm is required to obtain a curve that is distinguishable upon superposition.

(b) Using the exponentially decaying fit function for the scattering efficiency (arXiv paper), we show the convoluted D band intensity for width values of 1 nm (red) and 20 nm (blue), as shown in the inset. The offset due to the increased width is much more pronounced, resulting in this fit function yielding increasingly inaccurate results for larger widths unless the edge position is permitted to vary during the least-squares fit.