Sublimation Kinetics for Individual Graphite and Graphene Nanoparticles (NPs): NP-to-NP Variations and Evolving Structure-Kinetics and Structure-Emissivity Relationships

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ABSTRACT: A single nanoparticle (NP) mass spectrometry method was used to measure sublimation rates as a function of nanoparticle temperature (T_{NP}) for a number of individual graphite and graphene NPs. Initially, the NP sublimation rates were ~400 times faster than that for bulk graphite, and there were large NP-to-NP variations. Over time, the rate slowed substantially, though remaining well above the bulk rate. The initial activation energies (E_a) were correspondingly low and doubled as a few monolayer’s worth of material were sublimed from the surfaces. The high initial rates and low E_a are attributed to large numbers of edge and other low coordination sites on the NP surfaces, and the changes are attributed to atomic-scale “smoothing” of the surface by preferential sublimation of the less stable sites. The emissivity of the NPs also changed after heating, most frequently increasing. The emissivity and sublimation rates were anti-correlated, leading to the conclusion that high densities of low-coordination sites on the NP surfaces enhance sublimation but suppresses emissivity.

INTRODUCTION

Chemistry on the surface of nanoparticles (NPs) is important in catalysis and in many applications of polycrystalline nanomaterials, yet most measurements of nano surface chemistry average over many NPs or nano-crystallites. Because NPs in any ensemble are expected to have different distributions of surface sites (e.g., facets, vertices, defects, …), and in many cases, large variations in NP size and shape, there is reason to expect that the surface chemistry of individual NPs may deviate substantially from ensemble-averaged chemistry. Understanding these deviations, and associating them with variations in NP structure, is important in developing structure-reactivity relationships for nano surface reactions.

We have developed an approach to measuring reaction kinetics and emission spectroscopy for individual NPs, and here present the first application – to the sublimation kinetics for graphite and graphene NPs. We report on the NP-to-NP variations in the kinetics, the evolution of rates and activation energies (E_a) that occur as the NPs sublime, and on correlations between changes in the distribution of surface sites, and the brightness and wavelength dependence of the thermal emission spectra for individual NPs.

There have been many studies over the last 70 years of the equilibrium vapor pressure of graphite at temperatures >2300 K, including some with mass analysis of the vapor. The vapor consists of C_n clusters, with partial pressures in the following ratio: C_3 : C_1 : C_2 = ~77.4 : 20.2 : 2.4, with much smaller contributions from larger clusters. These data have been used to derive C_n heats of formation, ΔH(C_n), which are: C = 716.7 kJ/mol, C_2 = 837.7 kJ/mol, C_3 = 820.1 kJ/mol. Unusually, the sticking coefficients for C_n in collisions with hot graphite are well below unity, thus equilibrium data do not give the C_n sublimation rates or activation energies (E_a).

Graphite sublimation in vacuum has also been studied, providing total sublimation rates averaged over the C_n species and over the surfaces of the polycrystalline samples. As shown in Figure S1, an effective E_a for sublimation can be estimated by fitting the literature data to a rate law of the form R = A * exp(-E_a/kT), resulting in a value near 862 kJ/mol, substantially in...
excess of the C$_n$ $\Delta$H values. A laser-heated sublimation mass spectrometry study measured C$_n$ species distributions.\textsuperscript{13} As in the equilibrium vapor, C$_3$ was the most abundant, but the C/C$_3$ and C$_2$/C$_3$ ratios were significantly higher than in the equilibrium vapor.

Both our graphite/graphene NPs, and the bulk graphite materials used in the above experiments, have distributions of exposed surface sites, including perfect basal planes, vacancies, and other basal plane defects, exposed basal plane edges, and for polycrystalline materials, grain boundaries. Previous results regarding the energetics of such sites and for site diffusion and annealing, are summarized in the Discussion. Fully-coordinated, basal plane sites are the most stable, hence have the highest E$_a$ for sublimation. Basal plane edges, vacancies, and other defects expose atoms in under-coordinated and/or strained geometries, with lower stabilities, hence lower E$_a$s for sublimation. Therefore, the sublimation rates and E$_a$s values for both bulk graphite and for our NPs are weighted averages over the distributions of exposed surface sites. The bulk measurements also averaged over large ensembles of crystallites in the polycrystalline samples.

Our single NP measurements are, in essence, looking at individual crystallites, thus allowing the effects of NP-to-NP heterogeneity on sublimation rates to be observed. In addition, as the NPs sublime, the site distributions evolve, and we are able to observe the effects of this structural evolution on the rates and E$_a$s. For the bulk measurements, enough material was sublimed to ensure that the rates, averaged over many crystallites, reached steady state. For individual NPs, one question is whether anything like steady state can be reached.

Finally, we previously observed that when graphite and other carbon NPs are heated above ~1900 K, the intensities of their emission spectra change significantly over time, sometimes brightening by up to a factor of two.\textsuperscript{14} Here we characterize the changes in NP spectral intensities and wavelength dependence as NPs sublime, and are able to extract a correlation between the emission brightness and the sublimation rate that provides insight into the structural factors that control emissivity.

**EXPERIMENTAL METHODS**

The instrument and methods used for trapping a single nanoparticle (NP), and for measuring its charge (Q), mass (M), and temperature (T$_{NP}$), have been discussed previously.\textsuperscript{14-16} In brief, electrospray ionization (ESI) is used to get charged NPs into the gas phase, and after passage through hexapole and quadrupole ion guides, the NPs are passed through a split ring-electrode electrodynamic trap (SRET),\textsuperscript{17} where single NPs can be trapped. Argon in the 1 mTorr range is added to damp NP motion. A radio frequency voltage of frequency, F$_{RF}$, and amplitude, $V_0$, is applied across the trap, creating an effective potential minimum at the trap center. Any NP that becomes trapped is heated by a laser focused through the trap, and trapping is detected by observing the thermal emission from the hot NP using a Si avalanche photodiode (APD).

A trapped NP undergoes simple harmonic motion about the trap center, with well-defined frequencies associated axial and radial motion. The axial frequency, $F_z$, is given by:

$$F_z = \left(\frac{|Q|}{M}\right)\left(\frac{\sqrt{2}V_0}{4\pi^2F_{RF}z_0^2}\right), \quad \text{Equation 1}$$

where $z_0 = 2.96$ mm. $F_z$ is measured every 30 seconds by a resonance excitation technique, thus giving Q/M. To determine Q, $F_z$ is measured repeatedly as a vacuum ultraviolet lamp is used to induce single electron changes in Q, resulting in $F_z$ steps that are fit to determine Q. $F_z$ measurement precision is $\pm 0.03\%$, which is sufficient to determine Q exactly for Q $\leq 70$ — typical of the small NPs studied here. Given Q, M can be extracted from the $F_z$ measurements. Spontaneous thermionic emission charge steps, sometimes seen at high T$_{NP}$, are taken into account in calculating M.

To measure kinetics, M is monitored vs. time as the NP is held at constant T$_{NP}$, or at a series of T$_{NP}$ values. The M vs. time data is fit to determine the mass-loss rate at each T$_{NP}$. Rates are expressed as numbers of C atoms lost per second, but note that our measurements provide no information about the desorbing C$_n$ species. The NPs were heated by a continuous 532 nm laser, loosely focused through the trap center, such that the beam waist was more significant than the amplitude of the NP motion. We previously showed that there are no significant differences if, instead, a 10.6 $\mu$m laser is used for heating.\textsuperscript{14} The laser power was measured and controlled in order to stabilize T$_{NP}$.

**Uncertainty in Mass Measurements:** For NPs with Q $\leq 70$ (most NPs here) we are generally able to determine Q exactly, and in that case, the uncertainty in the M values extracted from equation 1 is primarily due to the uncertainty in $z_0$, which depends on the accuracy.
with which the trap was machined and assembled. We estimate that this factor results in uncertainty in the absolute mass calibration of roughly \( \pm 1.3\% \). For a few of the larger NPs where \( Q \) was too large to determine exactly, there is additional uncertainty in the absolute mass calibration of roughly \( \pm 0.6\% \). The precision or relative uncertainties in comparing \( M \) measurements is much better, \( \sim \pm 0.18\% \), from a combination of the uncertainties in measuring \( V_0 \) and \( F_z \). Each sublimation rate was determined by fitting at least 20 mass measurements to extract the slope of \( M \) vs. time.

Uncertainties in the absolute mass calibration cancel, at least partially, for some quantities reported. In the NP volume ratios used to correct spectral intensities, the absolute uncertainty from \( z_0 \) cancels exactly. To allow rates to be compared for NPs of different sizes, we normalize them to a nominal NP surface area, calculated from \( M \), assuming spherical shape with bulk density \( 2.265 \text{ g/cm}^2 \).\(^{18} \) Thus, the area-normalized rates are proportional to \( \frac{\Delta M}{M^{2/3}} \), and the \( \pm 1.3\% \) uncertainty in absolute mass loss rate becomes \( \pm 0.4\% \) after area normalization.

**NP Temperature Determination:** Emission spectra covering the 600 to 1600 nm range were recorded every 30 seconds, simultaneously with the mass measurements, using an optical system that has been described previously, along with the calibration methodology, and the uncertainties in \( T_{NP} \) values.\(^{14,16} \) Briefly, light emitted by the trapped NP was collected and split into \( \lambda < 980 \text{ nm} \) and \( \lambda > 980 \text{ nm} \) beams, which were dispersed by a pair of spectrographs, equipped with cooled Si CCD and InGaAs photodiode array cameras, respectively. The sensitivity of the optical system vs. wavelength, \( S(\lambda) \), is measured using a CO\(_2\) laser-heated micro-thermocouple (type C) as a calibration emitter, allowing NP spectra to be corrected for non-idealities in the optical system.

The NP spectra are fit to a thermal emission model function consisting of Planck’s function for ideal blackbodies, multiplied by an emissivity function, \( \epsilon \):

\[
I(\lambda, T_{NP}) = \frac{2c \cdot \epsilon(\lambda, T_{NP})}{\lambda^4 \cdot \left( \exp\left( \frac{hc}{\lambda k T_{NP}} \right) - 1 \right)} \quad \text{Equation 2}
\]

The \( \epsilon(\lambda, T_{NP}) \) function accounts for deviations from ideal blackbody behavior due both to the properties of the emitting material (graphite, graphene) and to optical coupling with NPs much smaller than the emitted wavelengths. According to Mie theory, the emissivity for small spherical particles is:\(^{19} \)

\[
\epsilon(\lambda, T_{NP}) = \frac{8\pi r}{\lambda} \text{Im} \left( \frac{(n + ik)^2 - 1}{(n + ik)^2 + 2} \right) \quad \text{Equation 3}
\]

where \( r \) is the NP radius, and \( n + ik \) is the complex index of refraction of the material, which depends on both \( \lambda \) and \( T_{NP} \). Even for bulk materials, \( n \) and \( k \) are generally not known over our wavelength range at high temperatures, and for NPs there are additional factors such as quantum confinement and large numbers of surface sites that may affect the optical properties. Therefore, as is commonly done for carbonaceous NPs,\(^{20-24} \) we use a power-law approximation to the emissivity, \( \epsilon(\lambda) \propto \lambda^{-n} \), with \( n \) as a fitting parameter, and the thermal emission model function is:

\[
I(\lambda, T_{NP}) = \frac{K}{\lambda^{(4+n)}} \cdot \left( \exp\left( \frac{hc}{\lambda k T_{NP}} \right) - 1 \right) \quad \text{Equation 4}
\]

Here, \( K \) is a normalization constant, and the two parameters that affect the wavelength dependence are \( T_{NP} \) and \( n \). We estimated\(^{14} \) that the extracted \( T_{NP} \) values have roughly \( \pm 6.2\% \) absolute uncertainty, with \( \pm 2\% \) relative uncertainty in comparing \( T_{NP} \). Note, however, that the uncertainty arising from the use of the power-law approximation is unknown, and we can only note that the fits to the experimental spectra are quite reasonable.

**Other Experimental Considerations:** Steps taken to ensure that the NPs are pure carbon are discussed in the SI. The conclusion is that contaminants from ESI or from air exposure are desorbed long before the kinetics experiments start, and that metal contamination should be negligible. Figure S2 shows an experiment testing possible effects on sublimation rates from background O\(_2\). The worst-case effects are estimated to be \(< 5\% \) at our lowest \( T_{NP} \) where sublimation is slow, dropping to \(< 0.1\% \) above \( \sim 1950 \text{ K} \).

**RESULTS**

Sublimation kinetics were studied in a series of experiments on individual graphite and graphene NPs. We first show experiments on single graphite and graphene NPs to illustrate the types of raw data collected,
and the approach used to extract kinetics and emissivity properties. We then present just the extracted information for sets of graphite and graphene NPs, focusing on both NP-to-NP variability, and the evolution of NP properties as the NPs are heated to drive sublimation.

**Single NP Data:** Figure 1 shows an experiment in which a graphite NP with initial mass 38.9 MDa (~38 nm diameter, if spherical), was heated in a series of steps, from ~1800 K to ~2100 K. An initial period during which the NP was held at ~1300 K for Q determination is not shown. Gaps in the data indicate periods when TNP was unstable, and these periods were omitted from further analysis. With the exception of a few excursions, TNP was generally stable to ~±10 K (±0.5%) during the constant TNP periods, and even the largest excursions were only ~ 30 K (1.5%).

M and TNP were measured 30 to 50 times at each TNP set point. The TNP values in boxes are simply the averages over the time intervals indicated by the solid vertical lines. Mass loss rates were determined by linear fits to the mass records in the same time intervals, thus giving the average rates, shown in boxes, expressed as C atoms lost/second.

![Figure 1](image)

Figure 1: Typical sublimation kinetics experiment, in which a single graphite NP of initial mass of 38.93 MDa was heated in step-wise fashion from ~1800 K to ~2100 K, then back down to 1800 K. The temperatures and sublimation rates (given as C atoms/sec) indicated in boxes are the values averaged over the time intervals defined by the vertical black lines.

In addition to M and TNP, the figure shows the integrated emission intensity (emitted photons/second/sr over the 600 – 1600 nm range) and the value of the n parameter in the power law emissivity function. Note that n decreases as TNP increased, and then increased again as the NP cooled, indicating that emissivity is temperature dependent. Similarly, the integrated emission intensity, I, increased by a factor of ~2 as TNP increased by a factor of ~1.16 (~1800 to ~2100 K), corresponding to I ∝ TNP^{4.7}.

The sublimation rate increased with increasing TNP, as expected, however, the rates at similar TNP values measured during the heating and cooling phases of the experiment were significantly different. For example, at ~1807 K at the beginning of the experiment, the NP sublimed at a rate of 10.2 C/sec, while during the period with TNP ≈ 1804 K at the end of the experiment, the rate was only 0.96 C/sec. Decreases in sublimation rate were also observed for other temperatures, although in those cases the TNP values didn’t match as well during the heating and cooling phases, complicating the comparison. Note also that during the period at ~2091 K, there was a slow increase in TNP. Nonetheless, the sublimation rate slowed significantly. As NPs sublime, some rate slowing is expected due to reduction in NP surface area, however, the mass loss over the entire experiment was only ~9%, thus the surface area loss (∝ M^{2/3}) would have been on the order of 6 %. Clearly, this small surface area loss cannot account for rates slowing by up to an order of magnitude.

To allow kinetic and emission behavior to be compared for different NPs, it is necessary to convert the raw results into more concise and comparable form, and this process is summarized in Figure 2 for the NP in Figure 1. In this experiment, TNP was first ramped up, then back down, but for other NPs, different TNP programs were examined. In the summary figures and discussion thereof, we indicate the order and direction of the sequence of heat ramps applied to each NP as follows: 1st Ramp: Up, 2nd Ramp: Down, etc.

The inset to Figure 2 shows typical emission spectra (black points) measured during the 1st heat ramp, along with fits used to extract TNP and n. Figure 2A shows the variation of the integrated emission intensity with TNP. Ideal blackbody emission intensity scales with emitter surface area and the emissivity for small NPs (equation 3) introduces another factor of r, thus intensity should scale with r^3. Therefore, to compensate for the expected effects of decreasing NP mass during the experiment (and to allow comparisons between NPs with different masses), the intensities in all the summary figures have been scaled by the NP mass (∝ r^3). Note that the intensity increased and decreased with TNP, but the final intensity at 1800 K was ~15% higher than the intensity measured at the same TNP prior to the heat ramps. Figure 2B plots the n parameter, which decreased with increasing TNP, then recovered as the TNP dropped, but only to ~80% of its initial value.
These changes in intensity and n parameter indicate that in addition to driving sublimation, heating caused irreversible changes in the NP emissivity.

Figure 2C plots the sublimation rates measured at each TNP as the NP was heated then cooled. The rates and TNP values are simply the rates and temperatures averaged over the constant TNP intervals indicated by the vertical lines in figure 1. To correct for the ~6% surface area loss during the experiment, and to allow comparisons with other NPs, we would ideally normalize rates to the NP surface areas, but these are unknown. We have approximately area-normalized the rates assuming that the NPs are spherical with the bulk density, thus obtaining upper limits on the area-normalized rates, given as C/sec/nm². The data for both the 1st ramp up and 2nd ramp down are reasonably linear when plotted as ln(C/sec/nm²) vs. 1000/T, thus the fit lines can be used to extract activation energies, E_a, and prefactors, A, in rate expressions of the type: R = A exp(-E_a/RTNP). For this data, the E_a value extracted from 1st ramp up was 244 kJ/mol. During the 2nd ramp down, the rates are not fit well by a single E_a value. The three highest TNP points are reasonably well fit (red line) to give E_a = 595 kJ/mol, and the three lowest TNP points (dashed line) give 412 kJ/mol. In either case, compared to the 1st ramp up, the E_a's are substantially higher, and the rates at low TNP substantially lower, during the 2nd ramp down.

Figures 3 and 4 present similar data for a single graphene NP. In this case, TNP was subjected to three heat ramps: up, down, then back up. M dropped from 64 MDa to ~58 MDa, corresponding to ~9% total mass loss over a total time of ~8000 seconds – similar to the percent mass loss and time scale for the graphite NP in figures 1 and 2. The mass-scaled emission intensity for the graphene NP (figure 4A) was initially only about half that of the graphite NP (figure 2A), however, it increased by a factor of 3 in the 1st ramp-up (compared to a factor of ~2 for graphite), and decreased by only a factor of ~1.8 during the 2nd ramp down. In the 3rd ramp up, there was further brightening but only at the highest TNP. The n parameter (figure
4B) showed a similar pattern of substantial change between the 1st ramp up and 2nd ramp down, with only the highest TNP differing in the 3rd ramp-up. Again, there were large, only partially reversible changes to the NP emissivity when it was heated to high TNP.

We discuss the meaning of the extracted Ea values, below, after summarizing the results for sets of NPs.

First, however, we present two experiments monitoring kinetic and emission behavior over longer time periods at constant TNP. The top of Figure 5 shows data for a graphite NP held at 1300 K for nearly 20 hours. TNP was generally stable to within ±10K (±0.8%), but there were a few events where the TNP control algorithm became unstable, causing brief excursions of up to ~60 K (< 4%). The initial mass was ~103.6 MDa (~52.5 nm if spherical), decreasing 13.2% to 89.9 MDa over ~69,500 seconds, corresponding to an average sublimation rate of 0.0018 C/sec/nm². The rate (i.e., the slope of M vs. time) was generally steady, but there were a few fluctuations on the hour time scale, only some of which appear to be correlated with fluctuations in TNP. The integrated emission intensity, I, increased by a factor of ~2 over the course of the experiment while the n parameter increased by ~50%, with significant correlated fluctuations that appear to correlate with variations in the sublimation rate.

The bottom shows a similar experiment in which a graphite NP (initial mass 33.7 MDa, ~36.1 nm if spherical) was heated, initially to 1900 K ~2 hours, then at 2000 K for an additional ~4.4 hours.

Figure 4: Analysis of the graphene experiment in figure 3. A: Integrated emission intensity averaged over each constant TNP period. B: Emissivity parameter, n, averaged over each constant TNP interval. C: Area-normalized sublimation rate vs. TNP for each heat ramp, along with fits to extract the effective Ea values shown.
nm laser, but when $T_{NP}$ was increased to 2000 K, a cw CO$_2$ laser was used to help heat the NP. The CO$_2$ laser is less stable, and decreased the stability of $T_{NP}$, which, nonetheless, only fluctuated by ±40 K, (±2%) with standard deviation of 17 K (<1%). The total mass loss was ~23%.

During the 2000 K period, the sublimation rate slowed by ~67%, from an average of 51 C/sec over the first 10 minutes to 17 C/sec over the final 10 minutes, whereas the surface area (assuming spherical shape) would have decreased by only ~13%. Note also that there were significant fluctuations in the sublimation rate (e.g., at ~14,000 sec) that are not correlated with fluctuations in either $T_{NP}$ or the emission intensity. The emission intensity generally tracked the fluctuations in $T_{NP}$, as expected, but the intensity also slowly increased during each constant $T_{NP}$ period, although not as dramatically as it did in the 1300 K experiment. For this NP, the n parameter decreased with time at 1900 K but was roughly constant at 2000 K.

The observation that the sublimation rate slows as graphitic NPs are heated and that the rate slows by more than the expected loss in surface area was true for all four NPs in figures 1-5. In each case there also were irreversible changes in emissivity, including greater brightness and changes in the n parameter that describes spectral curvature.

**Comparison Data:** Figure 6 plots aggregated data for emission properties from 15 graphite NPs with initial masses ranging from ~5 to ~120 MDa (~19 to 56 nm, if spherical), and for 7 graphene NPs with initial masses ranging from ~10 to ~70 MDa. A consistent set of symbols is used in figures 6-8, with color and shape indicating particular NPs, and filling indicating the 1st, 2nd, or 3rd heat ramps. The arrows after the legend symbols indicate whether each heat ramp was up or down, i.e., to increasing or decreasing $T_{NP}$. For some experiments, indicated by open symbols, we were only able to run a single heat ramp (always up) before losing the NP from the trap. For most, two or more ramps were completed. The vertical scales are identical for the

![Figure 6](image_url)

**Figure 6:** A and B: Integrated emission intensity for all graphite and graphene NPs in each heat ramp. Consistent symbol shapes are used for each NP. The symbol fill indicates the heat ramp. The arrows in the legend indicate whether the heat was ramped up or down. C and D: Emissivity parameter n for each NP in all heat ramps.
the graphite and graphene NPs, allowing direct comparison of the emission properties.

The top half of the figure shows the integrated emission intensities, scaled by the NP masses measured at the same time as the emission, i.e., approximately corrected for the effects expected from varying NP volume, both from NP-to-NP and for each NP as it sublimed. The main observations were:

1. The volume-corrected emission intensity increased with increasing T_{NP} for all NPs, but with substantial NP-to-NP variation.
2. One graphite and two graphene NPs stood out as having substantially higher-than-average volume-corrected emission intensities, even though their masses were similar to those of other NPs (see below).
3. The graphite and graphene NPs had similar emission intensities, i.e., while there were large NP-to-NP variations within each data set, the intensity ranges for graphite and graphene NPs overlapped.
4. Examples were seen where the emission brightness increased, decreased, or did not change significantly between the heat ramps.

The bottom half of figure 6 shows the analogous data for the n parameter, which controls the shape of the thermal emission model function used in spectral fitting. Low (high) n corresponds to flatter (sharper) λ dependence. The main points are that:

1. The n parameter tended to decrease with increasing T_{NP} but with NP-to-NP variation of more than a factor of 2.
2. The one graphite and two graphene NPs that had unusually high emission intensity also had unusually low n parameters, i.e., less λ-dependent spectra.
3. The graphite and graphene NPs had n parameters in overlapping ranges, but graphite had slightly higher n parameters on average.

Figure 7 summarizes the sublimation rates, R, plotted as ln(R) vs. 1000/T, such that the slopes are proportional to the activation energies (E_a). The data points are the experimental rates for each NP, and the lines are single exponential fits to the data. As in figures 2 and 4, the raw sublimation rates (C atoms/sec) have been normalized to the nominal NP surface areas, calculated assuming spherical shape with the bulk density.

The data are reported separately for the 1st heat ramp (always up) and for the 2nd and 3rd heat ramps, the direction of which can be seen in the legend for figure 6. The masses of the NPs in each heat ramp are shown in figure 8. Also plotted for comparison in each frame of figure 7 is an estimate of the sublimation rate for bulk graphite from measurements at temperatures above 2300 K.9-12 As shown in figure S2, those measurements are in good agreement and fit well by an Arrhenius expression, allowing the rate to be extrapolated into the slightly lower T_{NP} range here.

Most of the data are reasonably well fit by single exponential functions, but during the 1st heat ramps, the fits for some NPs deviate by up to a factor of ~5 at the lowest or highest T_{NP} points. In those cases, the fit lines shown are the best single exponential fits to the remaining points. In the 2nd and 3rd ramps, the data are generally well fit by single exponential rate laws.

To facilitate comparisons between different heat ramps and with the rates for bulk graphite, we also show the ensemble-averaged rates as solid red dots with red fit lines. Calculating the ensemble averages is complicated by the fact that the measured T_{NP} values varied from NP-to-NP. To obtain the average rate, we used the single exponential fits to each NP data set to estimate what the rates for each NP would have been at 1800, 1900, 2000, and 2100 K. These estimated rates were ensemble-averaged to obtain the red dots, which were then fit to single exponentials (red lines).

There are several important points to note:

1. During the 1st heat ramp, the average area-normalized rate for graphite NPs at 1800 K was ~400 times faster than the bulk graphite rate, and that for graphene was ~360 times faster. Our assumption of spherical shape in calculating the NP surface area gives an upper limit on the rate per nm², however, the actual NP surface areas are certainly not underestimated by anything like a factor of 400. Thus, we conclude that the NPs had substantially higher inherent sublimation rates per unit area than bulk graphite.
2. The NP sublimation rates increased more slowly with increasing T_{NP} than that for bulk graphite, such that for T_{NP} = 2100 K, the averaged NP rates were only a factor of ~three higher than that for bulk graphite.
3. The anomalously bright graphite NP (red circles) had the slowest sublimation rates, and the steepest slope of any of the graphite NPs. The two anomalously bright graphene NPs (red circles, blue triangles) also had somewhat steeper-than-average slopes, but still had higher-than-average sublimation rates.
4. The rates at low T_{NP} in the 2nd and 3rd heat ramps were substantially lower than those in the 1st heat ramp,
although still substantially higher than the bulk graphite rate. For example, at 1800 K the averaged rate for graphite NPs in the 2nd heat ramp was ~6.6 times slower than in the 1st heat ramp, but still ~60 times higher than that for bulk graphite.

5. The rates in the 2nd and 3rd heat ramps increased substantially faster with $T_{NP}$ compared to the 1st heat ramp so that for $T_{NP} > 2100$ K, the rates for all three heat ramps were similar and also similar to that for bulk graphite.
6. The area-normalized rates at low $T_{NP}$ in the different heat ramps varied from NP to NP by factors of up to 10 for the graphite NPs, and by factors of up to 20 for the graphene NPs. The variability of the rates decreased at higher $T_{NP}$ but still exceeded a factor of 4.

7. The NP-to-NP variability in the sublimation rate was much larger than the differences between the ensemble-averaged rates for graphite and graphene, i.e., there was no significant difference between graphite and graphene NPs.

Finally, the activation energies ($E_a$) and prefactors ($A$) extracted from the single exponential fits in figure 7 are plotted in figure 8 against the NP mass, measured at the beginning of each heat ramp. For NPs where only a single heat ramp was completed, just a single point is shown (open symbols). For NPs where multiple ramps were completed, filled symbols connected with lines are used. For a few of the more massive NPs, arrows are superimposed on the lines to show the order of the heat ramps (1 $\rightarrow$ 2 $\rightarrow$ 3). For other NPs, the $E_a$ and $A$ values can be associated with the 1st, 2nd, and 3rd heat ramps by recognizing that the NP mass always decreased from 1st to 2nd to 3rd heat ramp. The NP-ensemble-averaged $E_a$ and $A$ values, and the values for bulk graphite are shown as horizontal dashed lines.

The important points for this figure are:

1. There were no obvious trends in $E_a$ or $A$ with NP mass.

2. The $E_a$ values for both graphite and graphene NPs in the 1st heat ramps varied significantly from NP-to-NP, but many were unexpectedly low, resulting in ensemble-averaged $E_a$s of 322 kJ/mol for graphite NPs and 302 kJ/mol for graphene NPs, compared to $\sim 862$ kJ/mol for polycrystalline bulk graphite.

3. In the 2nd heat ramp, the $E_a$ values increased for all NPs, with the largest increases for those NPs with particularly low $E_a$ values in the 1st ramp. The ensemble-averaged $E_a$s increased to 487 kJ/mol and 364 kJ/mol for graphite and graphene, respectively.

4. In the 3rd heat ramp, the $E_a$ values for a few of the graphite NPs approached the bulk graphite value, but most remained well below, and for a few NPs, the $E_a$s decreased, in one case substantially. As a result, the average $E_a$ decreased slightly for graphite.

5. On average, the $E_a$ values for graphene NPs were lower than those for graphite NPs, but the differences were much smaller than the NP-to-NP variations within each data set. The same is true for the $A$ values.

6. For many of the NPs, the log of the $A$ values showed a pattern of changes with heat ramping very similar to the changes in $E_a$.

DISCUSSION

The results presented here show that there are substantial NP-to-NP variations in volume-scaled emission intensities, $n$ parameters, area-normalized sublimation rates, activation energies, and prefactors, and that all these properties evolve significantly as the NPs sublime. It is not obvious what factors influence the emission properties, however, the sublimation kinetics clearly must depend on the distribution of sites present on each NP’s surface. Sites with different structures will have different $E_a$s for sublimation, hence different rates. The substantial NP-to-NP variation in sublimation behavior is attributed to the heterogeneity of the graphene and graphite feedstocks, which have distributions of size, shape, and presumably of atomic-scale surface structure. The mass losses during each experiment correspond to removing several monolayer’s worth of material, thus it is reasonable to expect that the surface structures should evolve, thereby accounting for the observed evolution of the kinetics. Before discussing the structure-kinetics relationship, we need to consider two other properties which varied significantly from NP-to-NP, and thus could conceivably have affected sublimation: the NP size/mass and the charge.
**Effects of NP Mass on Sublimation Rates:** Figure 7 shows that the surface-area-normalized rates for the NPs in each heat ramp varied substantially and that they changed from one heat ramp to the next. The mass of each NP at the start of each heat ramp can be identified by comparison to figure 8, where the same symbols are used. Close examination shows no correlation between mass and rates in the 1st heat ramp – some NPs with similar masses had very different rates, and some NPs with very different masses had similar rates. In the 2nd and 3rd heat ramps, the NP-to-NP rate variations were smaller, and one apparent anomaly emerged. Most of the graphite NPs had rates within a factor of ~two of the average rate, and these showed no correlation to the NP mass. One graphite NP (turquoise pentagons) had distinctly higher rates, and it happened to be the lowest mass graphite NP (initial mass ~17.5 MDa) for which multiple heat ramps were completed. Note, however, that there were four other graphite NPs with an initial mass just a few percent higher, and these had rates at or below the average. Therefore, we discount the possibility that the high rates for this NP resulted from an inherent effect of mass on sublimation.

**Figure 8** plots $E_a$ and $A$ vs. NP mass, which varied by more than a factor of 20 across the distribution of NPs. Comparing the $E_a$ and $A$ values for each heat ramp across the ensemble of NPs shows substantial variations from NP to NP, but no obvious correlation with mass. It is true that the $E_a$ and $A$ values generally increased during the three heat ramps, while $M$ decreased, but the changes in $E_a$ and $A$ are attributed to evolution of the NP surface site structure rather than to any inherent effect of the small changes in mass.

**Effects of NP Charge on Sublimation Rates:** In these experiments, the NP charge, Q, varied from $+30e$ to $+110e$, generally increasing with NP mass. We previously showed that changing Q has no effect on emission spectra or TNP,14 and here the question is whether Q might have effects on sublimation kinetics. In fact, such effects would be quite surprising because Q/M is so low – between $7 \times 10^{-7}$ and $6 \times 10^{-6} \text{ e/Da}$, corresponding to between $8 \times 10^6$ and $7 \times 10^5 \text{ e/carbon atom}$. **Figure S3** shows the measured $E_a$ values for the graphite NPs plotted against the Q values measured at the beginning of each heat ramp. A comparison of figures 7 and S3 allows the rates for each graphite NP to be associated with its charge. As discussed in the SI, we conclude that there are no direct effects of Q on either sublimation rates or extracted $E_a$ values.

**Effects of NP Surface Site Distributions on Sublimation Rates:** For graphitic NPs, the two major classes of sites are perfect basal planes where all atoms are fully coordinated with unstrained bonds, and less stable sites such as basal plane defects or edges. Because such sites are less stable, they have lower heats of sublimation, and because they have fewer or strained C-C bonds, the transition states for sublimation should also be lower in energy (i.e., lower $E_a$s), compared to those for loss of C$_a$ from perfect basal planes.

For both graphite and graphene NPs, the rates measured at low $T_{NP}$ during the 1st heat ramps averaged about 400 times faster than the rate for bulk graphite, indicating that the NPs initially had large numbers of defective or under-coordinated surface sites. At low $T_{NP}$ during the 2nd heat ramps, the rates were much lower, indicating that the numbers of defective/under-coordinated surface sites decreased when the NPs were heated, driving sublimation. For most, but not all NPs, the rates in the 3rd heat ramps were slower yet, indicating that sublimation tends to drive the NPs toward more stable surface structures.

This evolution of the surface site distributions explains why the $E_a$ values extracted from the 1st heat ramp rate data were so low – below 300 kJ/mol for many NPs. Such low $E_a$ values are unphysical because any such sites would have sublimed away long before the start of the kinetics experiments, during the >20 minutes that each NP was held at ~1300 K for Q determination. For example, assuming a 1st order desorption rate constant of the form, $k_1 = v_1 \exp(-E_a/RT)$, and $v_1 \approx 10^{14} \text{ sec}^{-1}$, in the range typically seen for surface desorption,25-26 we can estimate the lifetime $(1/k_1)$ for a site with $E_a = 300 \text{ kJ/mol}$ to be ~10 msec at 1300 K.

Instead, the low 1st heat ramp $E_a$s reflect the evolution of the site distribution during the heat ramp. Initially, the NPs had a large number of sites contributing to sublimation, resulting in high initial rates, but as the coverage of such sites decreased during the heat ramp, the rate increased more slowly with $T_{NP}$ than would have been the case for a constant site distribution, artificially depressing the $E_a$ values extracted by fitting the slopes in figure 7.

The measured rates can be used to roughly estimate the average $E_a$ for sites contributing to sublimation during the 1st heat ramp. At 1800 K, the average mass loss rate was ~0.002 C/sec/nm$^2$, corresponding to an average surface atom lifetime of ~50 seconds. Using the $k_1$ expression given above, this would imply $E_a \approx 540$
kJ/mol, averaged over the sites contributing to sublimation. By the end of the 1st heat ramp, at ~2100 K, the average rate was ~0.04 C/sec/nm², implying an average surface atom lifetime of ~2.5 seconds and Ea ≈ 580 kJ/mol, consistent with the conclusion that the surface site distributions evolved to higher average site stability. These ~500 kJ/mol values are useful for comparison to what is known about the energetics of different graphitic sites and diffusion processes.

The net energy to remove an atom from a perfect basal plane, creating a mono-vacancy, is reported to be in the 705 to 725 kJ/mol range, and removing C₂ to create a di-vacancy has net formation energy estimated to be in the 700 - 790 kJ/mol range. It is likely that the Eₐ for these processes are higher yet, thus, under our conditions, sublimation of C or C₂ from perfect basal plane sites should make only minor contributions to the total rate. We were unable to find energetics for loss of larger Cₙ from basal planes, but given the numbers of bonds that would have to be broken, these are also likely to be minor processes under our conditions.

There are many types of defective sites that could contribute to sublimation under our conditions. While the creation of basal plane defects is probably not important in our TNP range, if the NPs have pre-existing basal plane defects, desorption of Cₙ from sites around the defects should have lower Eₐ, and could be significant if the numbers of such defects are large. Conversely, adatoms on top of graphitic basal planes are probably not important, because they are bound by only 145 to 200 kJ/mol and have Eₐ's for lateral diffusion in the 34 to 51 kJ/mol range. Therefore, any adatoms initially present on the NPs would have desorbed or diffused to defects or edges long before the start of our experiments.

The types of defective/under-coordinated sites that must occur in large numbers for NPs, are basal plane edges. Several symmetric edge structures are possible, including “armchair” with formation energy estimated to be in the range of 110 - 250 kJ/mol per angstrom of edge length, “zigzag” (116 - 300 kJ/mol/angstrom), and Klein (172 kJ/mol/angstrom). Armchair edges expose pairs of doubly coordinated atoms, zigzag edges expose individual doubly coordinated atoms, and the Klein edge exposes a row of singly coordinated atoms. In addition, there are lower symmetry edge structures that can form by reconstruction from the symmetric edge structures with low Eₐ's (< 200 kJ/mol). Thus, interconversion between different edge structures should be rapid on our time scale.

NPs necessarily have a large number of edge sites on their surfaces, around the basal plane perimeters (see SI) and at edges that form as material sublimes around basal plane defects, leaving holes in the basal plane. Because edge sites are numerous on NPs and have high formation energies, hence low sublimation Eₐ's, we conclude that they must make the major contribution to the sublimation rates.

An obvious question is the extent to which annealing is important during sublimation, i.e., is annealing fast enough to significantly modify the surface site distribution, as it evolves during sublimation? The Eₐ for lateral diffusion of C atoms within perfect basal planes is estimated to be in the ~675 to 780 kJ/mol range, and annealing of dislocation loops by a vacancy creation/migration mechanism has Eₐ ~800 kJ/mol, both substantially higher than the Eₐ's for NP sublimation. As already noted, interconversion between different edge structures should be fast, however, that simply converts between different types of under-coordinated sites with similar energies, rather than reducing their numbers. If the NPs have existing mono-vacancies, their Eₐ's for lateral diffusion are only ca. 115 to 135 kJ/mol, which would give diffusion rates fast compared to sublimation. Diffusion of a mono-vacancy to a basal plane edge is energetically favorable (and for NPs, the distances are small), and since this effectively heals the vacancy, we expect mono-vacancies to be short-lived. Note, however, that merging two mono-vacancies to form a di-vacancy is also energetically favorable, and the energy for lateral diffusion of di-vacancies is estimated to be 580 - 840 kJ/mol, i.e., once formed, di-vacancies are much more stable with respect to diffusion than mono-vacancies. This is presumably also true of larger vacancies. We conclude that atomic-scale transformations (mono-vacancy diffusion, edge interconversion) should be fast on the sublimation time scale, but that large scale restructuring of the NPs in ways that would significantly change the number of under-coordinated surface sites, is probably not. Therefore, sublimation – specifically preferential sublimation from defective/under-coordinated sites – is the dominant process driving the evolution of the surface site distributions during sublimation.

As shown in figure 8, in the 3rd heat ramps, the Ea values for a few of the NPs approached that for bulk graphite, but the average remained substantially lower, raising the question of how best to compare our single NP measurements, with the bulk sublimation experiments described above. The bulk experiments, on
polycrystalline graphite, would also have had contributions from a range of sites, including basal planes, exposed basal plane edges or defects, and grain boundaries. Furthermore, the individual crystallites in the bulk graphite undoubtedly evolved with time, similar to the evolution shown here for single NPs. The bulk rates averaged over many crystallites, however, and because macroscopic amounts of material were sublimed, the average site distributions and associated kinetics would have reached steady state at each temperature.

The obvious question is whether steady state can ever be reached during sublimation of individual graphite or graphene NPs. Consideration of graphitic NP structures, and of experiments like those in figures 5, 7, and 8, suggest that the answer may be “only partially”. Note that in the 1300 K experiment at the top of figure 5, the sublimation rate was reasonably steady (even though the emissivity changed substantially), but there were small rate fluctuations even in time periods when $T_{NP}$ was quite stable. For the higher $T_{NP}$ experiment, the rate varied substantially, generally slowing as the NP lost mass, however, there were several periods when the rate accelerated or fluctuated significantly, with no obvious correlation to changes in $T_{NP}$. Figures 7 and 8 also show a tendency of rates to slow and $E_a$s to increase as sublimation proceeds, corresponding to the evolution of the NP surface sites toward greater stability, however, this evolution is not monotonic. There were a few NPs where the rates accelerated and $E_a$s decreased in the 3rd heat ramp. This behavior suggests that there is a propensity for NP structures to evolve in ways that generally decrease the number of defective or low coordination surface sites, but that it is possible for there to be temporary increases in the number of such sites.

Consider graphitic NPs that are initially rough, with irregular edges, defects, and surface asperities. Such features have high densities of defective and low coordination sites, thus sublimation at these features should be fast, consuming them and leaving behind “smoother” NPs with fewer defective and low-coordination sites. Therefore, for such NPs, we would expect the sublimation rates to slow with time, as is typically the case here. On the other hand, it is also possible for the numbers of defective/low coordination sites to increase during sublimation. Consider idealized NPs with no basal plane defects and low coordination sites only at basal plane edges. For such NPs, sublimation at the exposed edges would shrink the basal planes, and because the basal plane area ($\propto d^2$, where $d$ is the lateral basal plane dimension) shrinks faster than the edge length ($\propto d$), the fraction of exposed edge atoms would increase. If the basal planes also have vacancies or other defects, sublimation around the defects would tend to enlarge them, further increasing the fraction of defective/low coordination sites.

Thus, for rough NPs, we might expect that the sublimation rates should initially decrease rapidly (and $E_a$s increase), as preferential sublimation “smoothes” the NP structure. As this process proceeds, we might expect each NP to reach a near steady-state situation where the NP sublimes at a gradually slowing rate due to continued smoothing of the surface structure, punctuated by occasional rate accelerations as new basal plane defects are exposed or created. Eventually, in the limit of large mass loss, the area-normalized rate should start to increase again as $d$ becomes small, however, none of the experiments here reached that limit, because the total mass losses were <20%.

The motivation for studying both graphite and graphene NPs was to examine the effects of changing the ratio of basal plane area to basal plane edge length. As discussed in the SI, for idealized NPs of identical masses, the number of edge atoms would be roughly three times higher for graphite than for the ~5 nm thick graphene NPs studied here. For sublimation dominated by under-coordinated sites, we might, therefore, expect higher surface area-normalized rates for graphite NPs, compared to graphene NPs. In fact, however, there was no significant difference in the ensemble-averaged sublimation rates.

The unexpectedly high reactivity for graphene could reflect a higher density of defect or other under-coordinated sites, however, it is at least partially an artifact of the way the rates were normalized to the nominal NP surface areas, assuming spherical shape. This assumption gives consistent lower limits for the surface areas and upper limits on the rates, but clearly, the spherical approximation is worse for graphene than graphite. Thus, if it were possible to use the true NP surface areas in the analysis, the rates for graphene NPs would be lower than the rates for the graphite NPs, consistent with the expected smaller number of low-coordination edge sites in the graphene NPs.

**Correlations between Emission Intensity and Sublimation Rates:** Figures 1 - 5 show several examples in which the integrated emission intensity, $I$, increased after heating, and in those examples, the sublimation rate, $R$, also slowed significantly. This raises the ques-
tion of whether emissivity is correlated with the sublimation rate, and if so, what the correlation reveals about the factors that control graphitic NP emissivity. One way to extract such correlations would be to compare I and R for all the NPs before and after periods at high T_{NP} where significant mass loss occurred. The difficulty is that our control over T_{NP} is not (yet) adequate to hit exactly the same T_{NP} values in different heat ramps and for different NPs. Therefore, the following approach was used. The rates (figure 7) and emission intensities (figure 6) measured in each heat ramp for each NP, were fit to determine how they varied with T_{NP}, using I \propto T_{NP}^s and R = A \cdot \exp(-E_a/kT_{NP}), with s, A, and E_a as fitting parameters. The fits were then used to interpolate between the I and R measurements, to estimate the values for T_{NP} = 2000 K.

Because of the large NP-to-NP variation in both I and R, it is difficult to deduce much about correlations by comparing the I and R values directly, as shown in figure S4. The correlation is clearer if we compare changes in I and R for each NP after heating, because this cancels out the large NP-to-NP variations in absolute intensity and rate. Figure 9 plots the percent change in I vs. the percent change in R for each NP, comparing the interpolated 2000 K I and R values measured in the 2nd and 3rd heat ramps relative to those measured in the 1st. Filled symbols compare I and R values measured in the 2nd and 1st heat ramps, and open symbols compare the net change between the 3rd and 1st heat ramps, with circles and diamonds for graphite and graphene, respectively. Arrows connecting the symbols show how particular NPs evolved. There are a few unconnected points for NPs where only two heat ramps were completed.

It can be seen that most of the points lie in the upper left quadrant, i.e., there is a reasonably strong anti-correlation between changes in sublimation rate and changes in emission intensity, the most common behavior being for intensities to increase while rates decrease. The variation in sublimation rates is attributed to the sublimation-driven evolution of the NP surface site distributions. Therefore, figure 9 suggests that the emission brightness of graphitic NPs increases when the numbers of defective or low coordination surface sites are decreased. It is not surprising that the NP surface structure and emission properties should be correlated, because defects and low coordination surface sites must affect the NP electronic and vibronic (phonon) state distributions. Understanding the structure-emissivity relationship quantitatively would appear to be an interesting topic for theoretical investigation.

CONCLUSIONS

We have, for the first time, reported sublimation rates as a function of temperature for individual graphite and graphene NPs. The average rates per unit area were initially several orders of magnitude faster than that for bulk graphite but decreased significantly as sublimation was driven at high T_{NP} over the course of several hours. There were, however, large NP-to-NP variations in the rates – much larger than the difference between the graphite and graphene rates, for example.

No significant correlations were observed of sublimation rates with NP mass or NP charge, both of which varied significantly as the NPs were repeatedly heated. Instead, the NP-to-NP variations in sublimation kinetics are attributed to the heterogeneity of the NPs and the resulting variations in the numbers of defective/under-coordinated surface sites. The evolution of the kinetics as the NPs were heated is, therefore, attributed to the evolution of the surface site distributions driven primarily by preferential sublimation from less stable sites.

The activation energies extracted from the rates increased substantially in repeated heat ramps, reflecting the evolution of the NP surface structure toward greater stability, however, the evolution during both repeated temperature cycling and in long term heating experiments was non-monotonic. The NPs approached a partial steady state in which their surfaces had relatively
stable fractions of low coordination and defect sites, but individual NPs never reached a true steady state.

The thermal emission intensity underwent only partially reversible changes as the NP temperature was repeatedly cycled. Most commonly, the emission brightened after heating, while the sublimation rates decreased, suggesting that emission intensity is depressed by high coverage of defects and low coordination surface sites.

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ABBREVIATIONS

NP, nanoparticle; TNP, nanoparticle temperature;

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Supporting Information

Bulk graphite sublimation

Figure S1 presents measured graphite sublimation rates and a fit to an Arrhenius rate law, \( R = A \exp(-E_a/kT) \), used to extract an \( E_a \) of 862 kJ/mol, and to extrapolate the rate to the \( T_{NP} \) range of our experiments. For materials where the sticking coefficients are unity, sublimation rates can be calculated from the equilibrium vapor pressures, and the figure also shows the rates obtained if this assumption is erroneously used in conjunction with measured equilibrium vapor pressures.\(^2\)

In fact, however, graphite has \( S \) values for sticking of various \( C_n \) vapor species that are well below unity.\(^3\)\(^-\)\(^5\) For example, \( S(C) \) was found to vary from 0.7 ± 0.15 at \( T_{surface} = 800 \) K, to 0.4 ± 0.2 at 2300 K,\(^3\) and \( S(C_3) \) was found to be zero within experimental uncertainty, for surface temperatures above 1000 K.\(^3\)\(^,\)\(^5\)

Figure S1. Measurements of the sublimation rates for graphite in vacuum by Clarke et al.\(^1\), Marshall et al.,\(^6\) Tsai et al.,\(^7\) and Haines et al.\(^8\). The solid line is an Arrhenius fit to the Clarke data. The orange points and dashed fit line show the sublimation rate that would \textit{incorrectly} be estimated if equilibrium vapor pressure data (in this case, by Zavitsanos et al.\(^2\)) are analyzed using the common, but in this case, erroneous assumption that the \( C_n \) sticking coefficient is unity with hot graphite surfaces. Note, Zavitsanos et al. did not make this error – the mis-estimate of the sublimation rate is included only to make the point that graphite sublimation is quite different from that typical for metals.
Graphite and Graphene NP purity in the experiments

The NPMS method only monitors the total NP mass, thus it is important that we work with materials with the highest possible purity, with particular concern regarding any contaminants (e.g., metals) that might catalyze sublimation or other reactions of interest. The entire ESI system is carefully cleaned whenever the NP material is changed, with parts exposed to the ESI solutions extensively cleaned or replaced. The graphite NPs examined here have stated purity of 99.9999% (metals basis, Alfa Aesar), and the graphene platelet material (US Research Nanomaterials, Inc.) has stated composition of 99.7% C, <0.3% O. As received, the NPs presumably have oxidized surface groups and adventitious adsorbates from air exposure. Electrospray ionization was done from 2 mM ammonium acetate solutions in methanol, thus the electrosprayed NPs likely also have excess ammonium acetate and methanol adsorbed. Molecules like water or methanol desorb at low temperatures, and ammonium acetate was chosen specifically because it decomposes to volatile products well below the $T_{NP}$ range of interest here.\(^9\) Similarly, oxidized surface groups have been shown to desorb as CO or CO\(_2\) below $\sim$1400 K when heated in vacuum.\(^{10-13}\) Trapped NPs are initially held at $T_{NP} \leq 1300$ K during charge stepping (20 – 60 minutes), then heated to 1800 K for the start of the sublimation experiments. We expect, therefore, both contaminants and heteroatom functional groups on the NP surfaces should have desorbed, i.e., the NPs should be quite pure.

Possible effects of background oxygen on the sublimation rates

Another consideration is that the presence of O\(_2\) or other oxidizers in the trap chamber background could lead to NP mass change from reactions, interfering with measuring sublimation rates. UHP Ar (99.999%) at pressures of $\sim$1 mTorr is used as a buffer gas to damp NP motion during normal operations, with UHV-compatible gas lines and fittings. The trap chamber is also
mostly UHV-compatible but because it is exposed to methanol from the ESI source during every NP injection, its base pressure is typically ~7 x 10^{-7} Torr. To test for the effects of small additions of O_2, experiments were done in which a separate flow controller was used to add O_2 to the Argon buffer gas at pressures ~1000 higher than the worst-case O_2 background pressure (i.e., assuming the background is air).

One such experiment is summarized in Figure S2, which presents a test of the effects of deliberately adding O_2 on the mass-loss rates. The mass-loss rates were measured without and with 0.18 mTorr of O_2 added to the argon buffer gas in the trap. From the difference in mass loss rates, the rate of oxidative mass loss can be determined. As has been observed previously^{14-15} the rate for graphite oxidation by O_2 decreases with increasing surface temperature in our T_{NP} range. As a result, in the worst case, where the O_2 pressure would have been ~10^{-4} of that used in figure
S2, background oxidation would have had < 5% effect on the sublimation rates at our lowest temperatures, decreasing with increasing T<sub>NP</sub> to < 0.1% above ~1950 K.

**Relation between NP charge (Q) and kinetics.**

**Figure S3** shows the Ea values for all the graphite NPs plotted vs. the Q value at the beginning of each heat ramp. The Q values tend to increase, particularly between the 1<sup>st</sup> and 2<sup>nd</sup> heat ramps, due to thermionic emission at high T<sub>NP</sub>. The inherent effects of Q can be judged by comparing the Ea values measured for each of the heat ramps across the ensemble of NPs. As with the situation for NP mass, the large variations in Q across the ensemble are clearly not correlated to the kinetics. For individual NPs, Q tends to increase in successive heat ramps, and Ea also increases, however, we believe these are simply the consequences of two unrelated processes that occur at high T<sub>NP</sub> – thermionic emission that increases Q, and sublimation that changes the surface site distribution, thus changing the sublimation kinetics. The effects of Q on

![Graph showing Ea vs Q](image-url)
the actual rates can be observed by comparing figure 7 and figure S3, which allows the Q value for each NP in figure 7 to be identified. Again, there is no correlation between Q and the rates.

Comparison of the fraction of under-coordinated edge sites for graphite and graphene NPs.

The sublimation rate for an NP is expected to be strongly influenced by the number of defective or under-coordinated sites exposed on the NP surface because such sites have lower stability, and therefore should have lower activation energy (E_a) for sublimation. For NPs, the class of such sites that clearly must be present in large numbers is edge sites. An idealized graphite NP might consist of a cubical stack of graphene layers. For example, given graphite’s 0.3353 nm interlayer spacing and 0.2461 nm basal plane unit cell edge length (2 C/unit cell),16 a stack with thickness of 100 layers would be ~33.53 nm thick, and if we assume square layers with 33.53 nm edges, then the resulting cubical NP would have mass of ~52 MDa – in the mass range for our NPs.

This cubical NP would have ~8.7 x 10^4 fully coordinated C atoms in the exposed top and bottom basal planes, and ~9.4 x 10^4 under-coordinated atoms in the edges of the stacked basal planes. Thus, for idealized graphite NPs with aspect ratios near unity, roughly 50% of the NP surface consists of under-coordinated atoms in basal plane edge sites. This ratio is independent of NP size but is strongly affected by the NP shape. For example, for the same NP thickness and basal plane area (i.e., the same mass), if the basal planes are elongated or irregularly shaped such that the perimeter/area ratio increases, the fraction of under-coordinated edge sites would also increase. On the other hand, if the NP is thinner, with fewer but larger basal planes (to keep the same mass), the fraction of edge sites decreases.

Consider graphene NPs. Our graphene NPs feedstock is stated to have 2 to 8 nm thickness, i.e., the average thickness is ~5 nm. A 5.03 nm thick NP would have 15 layers. If these layers
were square, they would need to have a lateral dimension of 86.5 nm to give the same 52 MDa mass as the cubical NP discussed above. In such a particle, there would be $\sim 3.6 \times 10^4$ under-coordinated atoms in the edges of the 15 stacked layers, with $\sim 5.8 \times 10^5$ fully coordinated atoms exposed in the top and bottom basal planes. Thus the idealized graphene NP would have only $\sim 6.3\%$ of its surface atoms in under-coordinated edge sites. More importantly, the total number of under-coordinated edge atoms would be about one third the number in an idealized graphite NP with an aspect ratio of 1.0.

Of course, real graphite and graphene NPs would have additional under-coordinated sites due to irregular shapes and to defects in the basal planes. Nonetheless, we expect that graphene NPs should have a significantly smaller fraction of under-coordinated surface atoms than graphite NPs, which should result in slower sublimation kinetics.

Another factor that must be taken into account in comparing the sublimation rates for graphite and graphene NPs is that the reported rates for each NP have been normalized to the nominal surface area, calculated as the surface area of a spherical particle with the same mass, assuming the bulk density. This sets a lower limit on the surface area, hence giving area-normalized rates that are upper limits. For the cubical NP discussed above, the actual surface area would be 1.23 times greater than the nominal area, and for the 5 nm graphene NP, the actual area would 1.68 times greater than the nominal area. Roughness or other irregularities would further increase the actual surface areas.

**Comparison of integrated intensities and sublimation rates in the three heat ramps.**

**Figure S4** plots the 2000 K integrated intensities vs. sublimation rates for all the NP. Because of the large NP-to-NP variations, it is difficult to see much correlation, other than a general tendency for sublimation rates to decrease in subsequent heat ramps.
Figure S4: Interpolated integrated intensities plotted vs. area-normalized sublimation rates, both at 2000 K, for all NPs where more than one temperature ramp was completed. On average, the rates decreased substantially from the 1st to 2nd heat ramps, and the NP-to-NP spread in emission brightness increased. Comparing the 2nd and 3rd ramps, the effects on rates and intensities were much smaller, making generalizations difficult.
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