

Supporting Information

Time-resolved Mass Spectrometry of Nano-Al and Nano-Al/CuO Thermite under Rapid Heating: A Mechanistic Study

Guoqiang Jian[†], Nicholas W. Piekiet[‡] and Michael R. Zachariah^{,†,‡}*

[†] Department of Chemistry and Biochemistry, University of Maryland, College Park, 20742,
United States

[‡] Department of Mechanical Engineering, University of Maryland, College Park, 20742, United
States

*Corresponding author, email: mrz@umd.edu.

S-I. Temporal evolution of water peak intensity of rapid heating of Al-NPs.

S-II. Temporal evolution of H_2O^+ , OH^+ , and H_2^+ peaks intensities of rapid heating of Al-NPs up to 1650 K in 3 ms.

S-III. Comparison of Al_2O and AlO species concentration in TOFMS.

S-IV. Estimation of background water flux in TOFMS.

S-I. Temporal evolution of water peak intensity of rapid heating of Al-NPs up to ~ 2000 K.

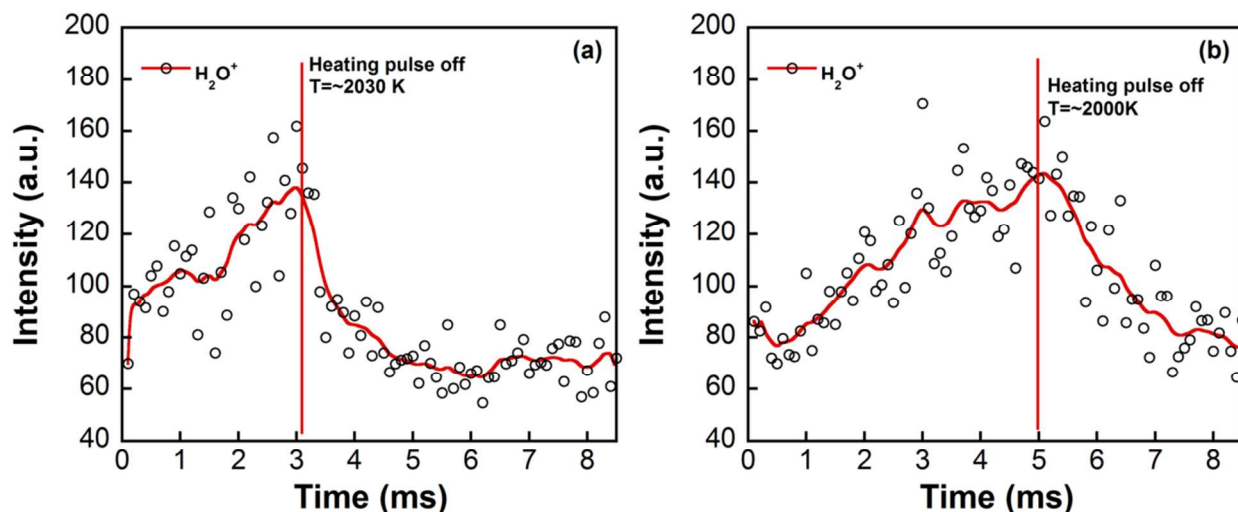


Figure S1. Temporal evolution of water peak intensity from rapid heating of Al-NPs (a) ~3 ms heating pulse (heating rate $\sim 3 \times 10^5$ K/s) and (b) ~5 ms heating pulse (heating rate $\sim 6 \times 10^5$ K/s).

In Figure S1a-b, we plot the temporal evolution of H_2O^+ peak intensity at two different heating pulse times (~3 ms and ~5 ms). From Figure S1a-b, we can see that the H_2O^+ peak increases as the temperature goes up in both cases, indicating the water release from the Al-NPs upon heating.

S-II. Temporal evolution of H_2O^+ , OH^+ , and H_2^+ peaks intensities of rapid heating of Al-NPs up to 1650 K in 3 ms.

We plot the temporal trends for H_2O^+ , OH^+ , and H_2^+ , as shown in Figure S2. No AlO_x , and O were found in mass spectra since the maximum temperature is 1650 K. Different trends of H_2^+ and OH^+ indicate that no water decomposition process happens here. We also want to point out that we have never observed H_2 signal in the background mass spectra as well as the rapid heating of bare metal oxide nanoparticle cases. However, the H_2 peak can be seen either in rapid

heating of Al-NPs or aluminum nanothermite cases, indicating the reaction of aluminum with water leading to the production of H_2 .

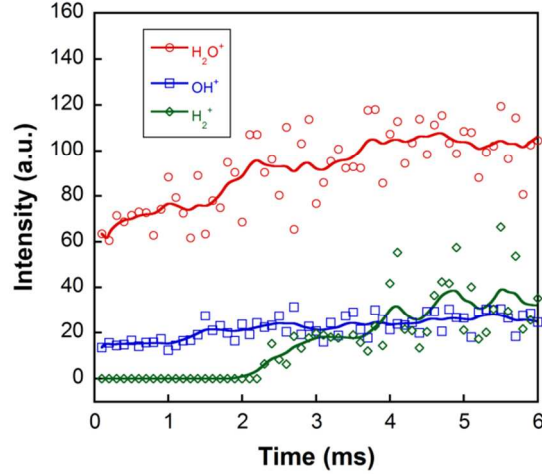


Figure S2. Temporal evolution of H_2O^+ , OH^+ , and H_2^+ peaks intensities of rapid heating of Al-NPs up to 1650 K in 3 ms.

S-III. Comparison of Al_2O and AlO species concentration in TOFMS.

By knowing the ionization cross section values for different species, we are able to calculate the partial pressures from the measured ion intensities based on the following equation Eq. (S1)

$$I_{Al} = A\sigma_{Al}C_{Al}, I_{Al_2O} = A\sigma_{Al_2O}C_{Al_2O}, I_{AlO} = A\sigma_{AlO}C_{AlO} \quad (S1)$$

A is the constant associated with the mass spectrometer, σ_{Al} , σ_{Al_2O} and σ_{AlO} are the electron-impact cross section, C_{Al} , C_{Al_2O} and C_{AlO} are the concentration of species. When electron beam is set at 70 eV, $\sigma_{Al} \approx 7.5 \text{ \AA}^2$, $\sigma_{Al_2O} \approx 11.8 \text{ \AA}^2$, and $\sigma_{AlO} \approx 4.8 \text{ \AA}^2$.

It is obvious that the cross section of AlO is less than half of the cross section of Al_2O . That means, for the same concentration of species, AlO peak in mass spectrometer should be less than

half of Al_2O species. However, as shown in Figure 1 at $t=3.3$ ms, Al_2O intensity is ~ 70 , while AlO intensity is ~ 13 . A rough calculation shows that the Al_2O concentration is ~ 2.2 times higher than AlO concentration.

$$70 = A \times 11.8 \times C_{\text{Al}_2\text{O}}, 13 = A \times 4.8 \times C_{\text{AlO}}$$

$$\frac{C_{\text{Al}_2\text{O}}}{C_{\text{AlO}}} \approx 2.2$$

S-IV. Estimation of background water flux in TOFMS.

Since H_2O is the main background species as we saw in Figure 1a, we need to consider the possibility of gas phase water reacting with aluminum. For our background pressure ($P \approx 4.2 \times 10^{-6}$ torr), the Knudsen number is $K_n \gg 1$, and we can estimate the water vapor flux using Eq. (S2),

$$J_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{N_A \sqrt{2\pi m k T}} \quad (\text{S2})$$

Here, $p_{\text{H}_2\text{O}}$ is the partial pressure of water vapor in vacuum, N_A is the Avogadro constant, m is the mass of a water molecule, k is the Boltzmann constant, and T is the temperature of the water vapor in vacuum. H_2O , N_2 and O_2 are the main three background species shown in Figure 1a, the intensities of these species are identified as $I_{\text{H}_2\text{O}}$, I_{N_2} , I_{O_2} . The observed ion intensities are related to the concentration through the ionization cross-section (at same temperature).

$$I_{\text{H}_2\text{O}} = A \sigma_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}, I_{\text{N}_2} = A \sigma_{\text{N}_2} C_{\text{N}_2}, I_{\text{O}_2} = A \sigma_{\text{O}_2} C_{\text{O}_2} \quad (\text{S3})$$

A is the constant associated with the mass spectrometer, $\sigma_{\text{H}_2\text{O}}$, σ_{N_2} and σ_{O_2} are the electron-impact cross section, and $C_{\text{H}_2\text{O}}$, C_{N_2} and C_{O_2} are the concentration of species. The calculated concentration of background species was then used to determine the partial pressure for each component, listed in Table S1.

Table S1. Estimation of Partial Pressure from Measured Intensity in Mass Spectrometer ^a

Gas Species	Intensity I (a.u.)	e-impact cross section σ ($\text{\AA}^2$) at 70 eV ^{S1}	Partial pressure p (Pa)
H ₂ O	~100	2.275	$\sim 3.8 \times 10^{-4}$
N ₂	~40	2.508	$\sim 1.4 \times 10^{-4}$
O ₂	~10	2.441	$\sim 3.4 \times 10^{-5}$

^a Pressure in ionization chamber is $P \approx 4.2 \times 10^{-6}$ torr $\approx 5.6 \times 10^{-4}$ Pa.

Using Eq. (S2), the water vapor flux J_{H_2O} is estimated to be $\sim 3.9 \times 10^{-31}$ mol/(cm².s). The extremely low flux rate of water vapor in the mass spectrometer indicates that the detected hydrogen production in the mass spectrometer could not be the result of reaction between the aluminum and gas phase water vapor, but rather absorbed water incorporated within the alumina shell.

S1. Kim, Y. K.; Irikura, K.K.; Rudd, M.E.; Ali, M.A.; Stone, P.M.; Chang, J.; Coursey, J.S.; Dragoset, R. A.; Kishore, A. R.; Olsen, K. J.; Sansonetti, A. M.; Wiersma, G. G.; Zucker, D. S.; Zucker, M. A. NIST Electron-Impact Cross Section Database, <http://physics.nist.gov/PhysRefData/Ionization/molTable.html> (accessed March 26, 2012).