Supporting Information for

Molecular dynamics study on evaporation of metal nitrate-containing nanodroplets in flame spray pyrolysis

Dingyu Hou[a], Geng Wang[a], Jingqi Gao[a], Kai H. Luo[a,*]

[a]*Department of Mechanical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK*

- **MD simulation of a pure water droplet for force field validation**

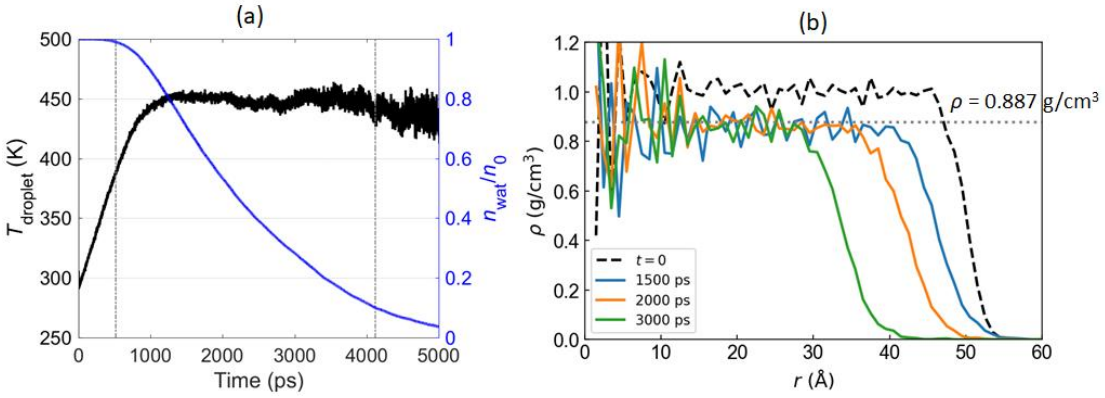

Figure S1 (a) Temporal evolution of the droplet temperature (left y-axis) and the number of water molecules within the droplet (normalized by the initial number of H_2O molecules n_0; right y-axis) during evaporation of a pure water droplet. (b) Radial distribution of mass density at different times during evaporation of a pure water droplet. The initial diameter of the water droplet is 10 nm. Ambient N_2 is at 1000 K.

- **Calculation of the diffusion coefficient of Ni^{2+} in bulk $Ni(NO_3)_2$ solution for force field validation**

Diffusion coefficient of Ni^{2+} in bulk $Ni(NO_3)_2$ solutions is calculated based on MD simulations. The solution temperature is 300 K. The water-salt-ratio (WSR; the ratio of the number of water molecules to the number of metal ions) is 50, corresponding to a concentration of 1.1 mol/L.

Figure S2 illustrates the initial simulation configuration of the bulk $Ni(NO_3)_2$ solution. Periodic boundary conditions are applied in all three directions. Detailed procedures of calculating the diffusion coefficient (D) of Ni^{2+} are as follows:

(1) Build the initial configuration of the bulk $Ni(NO_3)_2$ solution by randomly packing 300 Ni^{2+}, 600 NO_3^-, and 15000 H_2O (WSR = 50) within a cubic simulation box (46 Å × 46 Å × 46 Å) using the PACKMOL software.

(2) Equilibrate the solution at 300 K, 1 atm. The NPT ensemble (i.e., controlled particle number, pressure, and temperature) is used. Figure S3 shows the potential energy of the $Ni(NO_3)_2$ solution versus time, suggesting the system reaches equilibrium state after ~50 ps.

(3) After the solution reaches equilibrium state at 300 K and 1 atm, five equilibrated structures are randomly (in uniform distribution) selected as the starting configurations to run another 100 ps, during which the mean squared displacement (MSD) of Ni^{2+} is recorded.

(4) Diffusion coefficient D can be extracted from the fitted slope of MSD versus time as

$$\mathrm{MSD} \equiv \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle = 6Dt ,$$

where $\vec{r}(t)$ is the atom position at time t, $\vec{r}(0)$ is the reference position at $t = 0$, and D is the diffusion coefficient.

(5) Since MD simulations have statistical noise, D is calculated based on five different trajectories as described in step (3). The final D is the averaged results of the five replica runs. The standard deviation of the five replica runs is taken as the uncertainty of the calculated D.

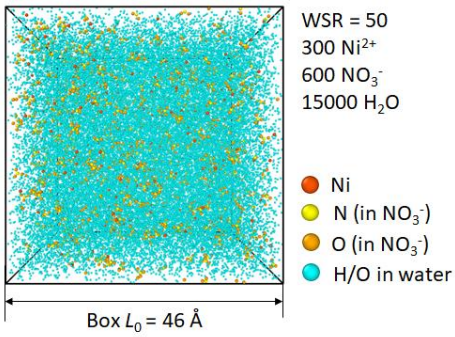

Figure S2 Initial simulation configuration of the bulk $Ni(NO_3)_2$ solution.

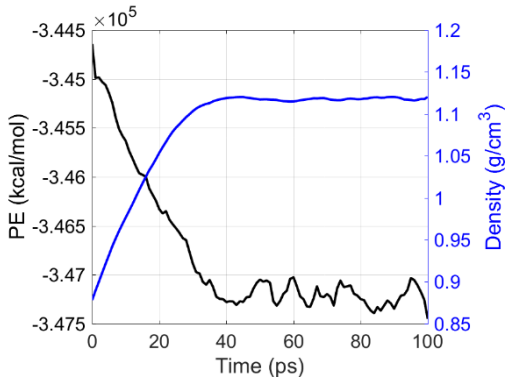

Figure S3 Temporal evolution of the potential energy (left y-axis) and mass density of the system (right y-axis) during equilibration of the bulk $Ni(NO_3)_2$ solution at 300 K.

- **Equilibration of a metal-nitrate-containing nanodroplet in vacuum at 300 K**

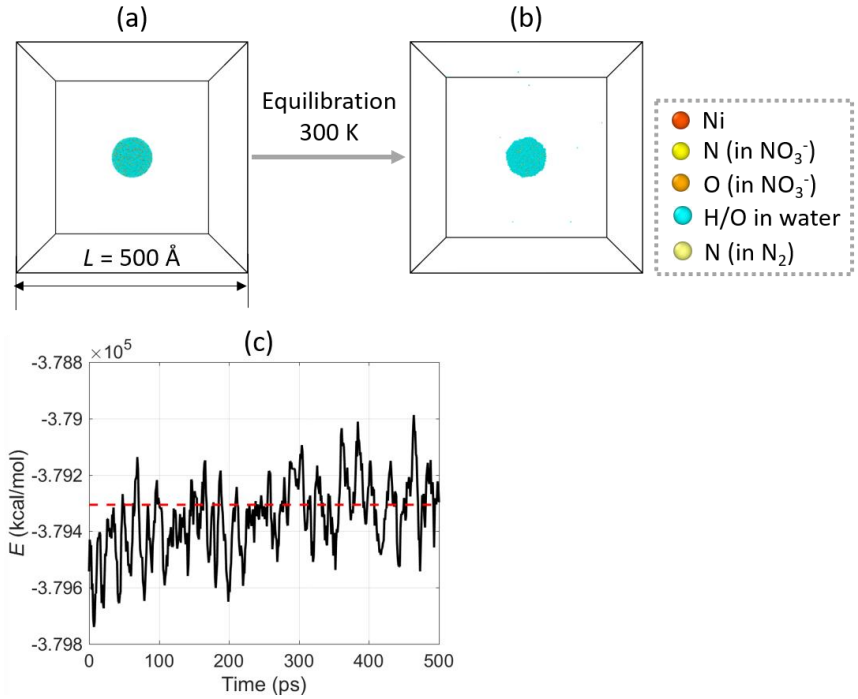

Figure S4 (a) Initial configuration of a 10 nm droplet composed of $Ni(NO_3)_2$ as the solute and H_2O as the solvent. The initial solution concentration is 1.0 mol/L; (b) Configuration of the $Ni(NO_3)_2$-containing nanodroplet after 500 ps equilibration at 300 K; (c) Potential energy versus time during equilibration of the $Ni(NO_3)_2$-containing nanodroplet at 300 K.

- **Radial distribution function of the Ni-O atom pair within a $Ni(NO_3)_2$-containing nanodroplet**

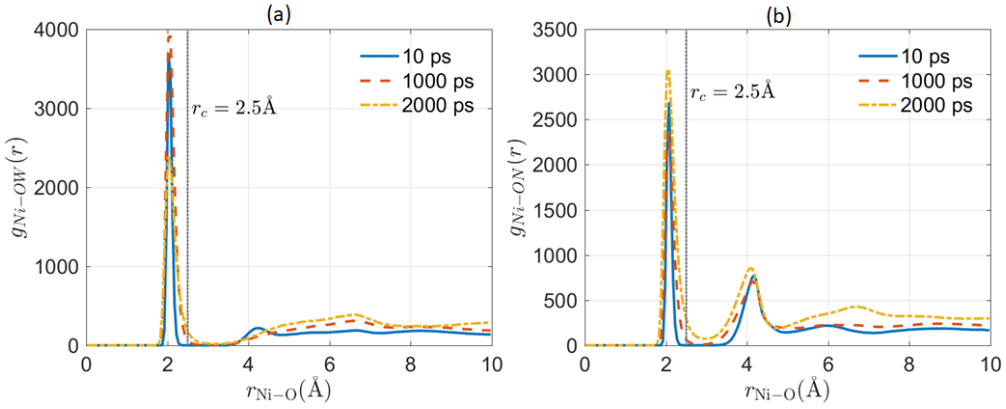

Figure S5 Radial distribution function (RDF) of Ni-OW (OW represents O atoms from water) atom pair (a); and Ni-ON (ON represents O atoms from NO_3^-) (b) at different times during evaporation of a 10 nm $Ni(NO_3)_2$-containing droplet. The initial solution concentration is 5.4 mol/L. Ambient N_2 is at 2500 K.

- **MD simulated evaporation rate constant**

Table S1 Evaporation rate constant K_{evap} (1E-8 m/s^2)[a] for a 10 nm $Ni(NO_3)_2$-containing droplet with

different initial solution concentrations (c = 5.4, 3.0, 1.0, and 0.0 mol/L) evaporating in ambient N_2 at various temperatures (T = 1000, 1500, 2000, 2500, and 3000 K).

T \ c	5.4	3.0	1.0	0.0[b]
1000	1.496±0.04944	1.931±0.03105	2.223±0.07795	2.423±0.06171
1500	2.585±0.06626	3.775±0.05871	4.447±0.1544	5.022±0.04239
2000	3.521±0.03857	5.648±0.08190	7.332±0.1403	8.711±0.08393
2500	4.206±0.1509	7.695±0.03102	10.864±0.2385	13.346±0.3030
3000	4.963±0.06451	9.577±0.06447	14.460±0.2822	19.293±0.4110

a. For each initial solution concentration and ambient N_2 temperature, K_{evap} is the averaged results of five replica runs with different initial configurations. The standard deviation of the five replica runs is taken as the uncertainty of the calculated K_{evap}.

b. An initial concentration of 0.0 means the evaporation of a 10 nm pure water droplet. K_{evap} for a pure H_2O droplet is obtained by fitting the squared droplet diameter d^2 and time t into the linear relationship using the data points between 1% and 90% H_2O molecules are evaporated.