

Single Nanoparticle Ion Trap (SNIT): A Novel Tool for Studying *in-situ* Dynamics of Single Nanoparticles

Sung Cheol Seo, Seung Kyun Hong, and Doo Wan Boo*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

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The development of high performance single nanoparticle ion trap (SNIT) apparatus for studying *in-situ* dynamics of single nanoparticles in controlled environments is described. The performance of SNIT apparatus has been evaluated for 500 nm SiO₂ particles. The mass resolution of ~100 ppm and the capability of varying the charge states independently have been demonstrated.

Key Words : Single nanoparticle, Ion trap, *in-situ* dynamics, Mass analysis

Introduction

In recent years, considerable interest has arisen in the study of chemical reactions and nanoparticles at the single molecule level in various environments.¹ The single molecule manipulation techniques often employed are based on scanning probe microscopy (SPM), such as AFM, STM, near-field scanning optical microscopy (NSOM) and their variations.² These SPM-based studies have advanced greatly our understanding of the chemical processes and properties of nanoparticles on surfaces.³ However, these techniques pose complexities in deducing the exact origins of molecular processes and nanoparticle properties due to the complicated nature of tip-sample and sample-surface interactions.

To overcome the intrinsic difficulties of the SPM-based methods, we developed a new single molecule manipulation method that can isolate single molecules and nanoparticles under controlled environments in the gas phase (in vacuum and ambient pressure) and monitor *in situ* the properties and reactions of single molecules and nanoparticles. The basic unit is based on the Paul ion trap,⁴ which is often used in conventional ion trap mass spectrometers.⁵ In our apparatus, called a single nanoparticle ion trap (SNIT), the trap structure and detection scheme are greatly modified from the conventional Paul trap for the efficient isolation and ultra-sensitive detection of single micro- and nano-sized particles. In this paper, we report the development of a single nanoparticle ion trap (SNIT) apparatus aimed at performing spectroscopy on single mass- and charge-selected molecules and nanoparticles, and its first application to single 500 nm SiO₂ nanoparticles.

Experimental Details

The SNIT apparatus is composed of two cap electrodes and one surrounding octapole, which is different from the conventional Paul trap (consisting of two cap electrodes and

one ring electrode). Due to the open structure of SNIT, our apparatus has the advantages of easy access to the trap center and high detection efficiency for low level scattering and fluorescence light. A home-made AC high voltage supply (4 kV_{p-p} max., 0.1 Hz-50 kHz) connected to two cap electrodes is used to generate effective harmonic potential for trapping charged nanoparticles. The DC-biased octapoles are used to compensate for the gravitational force and manipulate the horizontal and vertical locations of nanoparticles inside the trap.⁶

The trapped nanoparticles are irradiated by a home-made diode laser (675 nm, 5 mW) with a gaussian beam profile. The scattered light is collected by objective lens arrays in three orthogonal directions and then detected by two CCD cameras and one avalanche photodiode (APD) detector (Hamamatsu, model C5460-01). The ion trajectories monitored at the side and bottom of the trap by two CCD cameras are used to optimize the motions of trapped particles. The output from the APD detector is preamplified (× 100) and fed into a digital oscilloscope to determine the time evolution of scattered light intensity. Subsequently, the time-dependent signals are converted to the power spectrum in the frequency domain by using a fast Fourier transform (FFT) routine. The secular frequencies and their higher harmonic frequencies in the spectrum are then assigned to the corresponding secular motions. Combined with the predetermined trap geometry and potential parameters, the secular frequencies are used to determine the mass-to-charge (M/Q) ratio according to the relationship between the secular frequencies and M/Q values:

$$M/Q = \sqrt{2} V_0 / z_0^2 \Omega \omega_z, \quad (1)$$

where V_0 and Ω are the amplitude and angular frequency of AC voltages, and z_0 is the distance between the trap center and the hyperbolic front surface of cap electrodes (see ref. 7 for the details of principles).

To vary the charge states of trapped nanoparticles, a time-gated electron beam source consisting of a homemade electron gun (containing a tungsten filament, einzel lenses and deflectors), and a pulse generator with 100 μ s time

*To whom correspondence should be addressed. Tel: +82-2-2123-2632, Fax: +82-2-364-7050; E-mail: dvboo@alchemy.yonsei.ac.kr

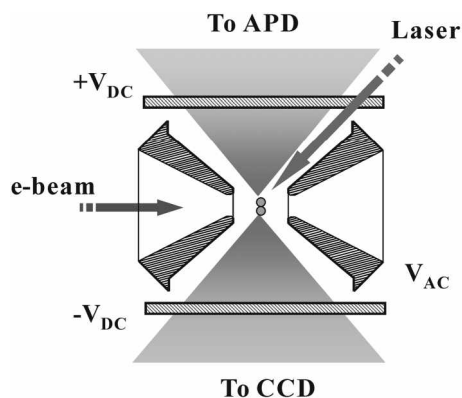


Figure 1. Schematic of the SNIT apparatus.

resolution was constructed and used for stepwise charging and discharging of nanoparticles. The secular frequencies at two different charge states, with the mass being maintained constant, were used to determine independently the mass and charge states. In particular, the changes in secular frequencies involving unit changes in charge states ($\Delta Q = \pm 1$) permit unambiguous assignment of absolute charge states of nanoparticles. Figure 1 shows the schematics of the constructed SNIT apparatus.

Results and Discussion

The standard 500 nm SiO_2 nanoparticles with the size distribution of 500 ± 40 nm (Merck Co., SEM image inserted in Figure 2) were used to evaluate the performance of the SNIT apparatus and study *in-situ* the gas-surface reactions on single isolated SiO_2 nanoparticles. The injection of SiO_2 particles into the trap was accomplished by using a particle dropping method. In this method, He carrier gas (1 atm) passes through the microchannel SiO_2 reservoir located at the top of trap, and expands *via* three pumping stages into the trap. Initially, several 500 nm SiO_2 nanoparticles were trapped and then ejected one by one by varying the DC potential of octapoles until a single stable SiO_2 particle remained. The entire ejection processes were monitored by two CCD cameras.

Trapped nanoparticles tend to have high kinetic energies due to their large mass, so their energies needed to be

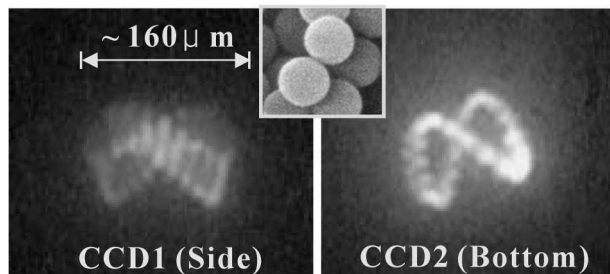


Figure 2. Ion trajectory images of single 500 nm SiO_2 particles captured by two CCD cameras at the side and bottom of the trap. The trap conditions are as following: 3095 V_{pp} , 1568 Hz, 20.6 V_{DC} . SEM image of 500 nm SiO_2 particles (inset).

dissipated to localize their motions near the trap center for better harmonic approximation. This goal was accomplished by introducing an instantaneous pressure jump inside the trap by a leak valve that damped the motions by collisional energy transfer to the background He gas. The ultimate pressure inside the trap was about 10^{-7} torr.

Figure 2 shows the trajectories of a single 500 nm SiO_2 nanoparticles captured simultaneously at the side and bottom of the trap by two CCD cameras. The pattern of trajectory and stability of motion depend strongly on various trapping conditions, such as the trapping potentials and frequencies, DC bias of the octapole, etc. Very crucial to the technique is optimizing the trapping conditions to maintain a stable secular motion of the particles to obtain the best mass resolution and accuracy of the SNIT apparatus. Under stable secular motion, the mass resolution and accuracy of SNIT apparatus is thought to depend mainly on the stability and accuracy of the electronics used in the experiment. The illustrated trajectories with ~ 160 μm size were obtained at 3095 V_{pp} , 1568 Hz, 20.6 V_{DC} octapole bias.

Figure 3 illustrates the stepwise charging and discharging processes of a single positively charged 500 nm SiO_2 particle by the time-gated electron beam (500 eV energy). The secular frequencies and charge states remain constant within the resolution of the measurement electronics employed (~ 100 ppm), changing only when the trapped particles are interrogated with an electron beam. The charge state of positively charged nanoparticles tends to increase *via* multi-electron emission by high energy electron bombardment, and in rare events (for instance, No. 72 in Figure 3) decrease *via* electron attachment of slow secondary electrons. Since the unfavorable electron attachment by slow electrons occurs predominantly *via* a single electron event involving the changes of charge states by unit charge ($+Q/e$), the differences in secular frequencies for charging steps are set to be integer multiples of the differences in secular frequencies of the electron attachment step (No. 72). The absolute mass and charge states of nanoparticles are determined separately on this basis. In this particular case in the present study, the mass of the 500 nm SiO_2 particle was determined to be $1.0618 (\pm 0.0001) \times 10^{-16}$ kg in close proximity of the previous measurement (1.3×10^{-16} kg).^{6,8} We believe that the

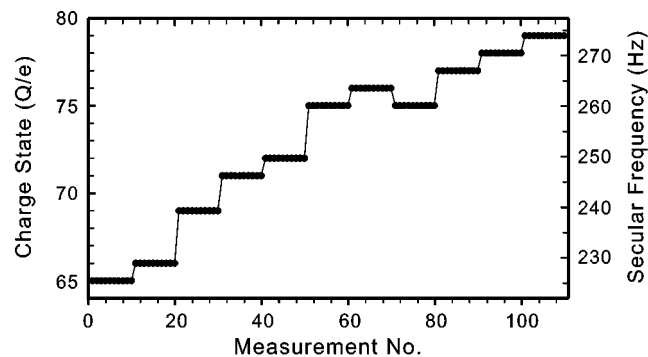


Figure 3. Stepwise charging and discharging of single positively charged SiO_2 particle by time-gated electron beam. Electron beam energy was 500 eV.

discrepancy in the two values is due to the size distribution of SiO₂ nanoparticles, not the inaccuracy of the SNIT apparatus.

The size range for nanoparticles trapped by our SNIT apparatus was 100 nm-50 μm, and the achieved mass resolution was ~100 ppm. With the incorporation of a fluorescence detection method, high frequency AC supply (up to 1 MHz), and high accuracy measurement instruments, the size range of 1 nm-50 μm and mass resolution of 1 ppm can be achieved. The current SNIT apparatus can be used to study *in-situ* the growth dynamics of carbon nanotubes on single catalytic nanoparticles, and also the fluorescence behavior of single quantum dot-silver nanoparticle composites in controlled environment. Such work is in progress.

In summary, the present study describes the development of a high performance single nanoparticle ion trap apparatus to study the *in-situ* dynamics of single nanoparticles and eventually single molecules in controlled environments. We have demonstrated the capability to trap 500 nm SiO₂ particles, varying independently the charge states of trapped nanoparticles, and determining the mass within ~100 ppm.

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References

1. (a) Basche, T.; Moerner, W. E.; Orrit, M.; Wild, U. P. *Single-Molecule Optical Detection, Imaging and Spectroscopy*; VCH Verlagsgesellschaft mbH: Weinheim, 1997. (b) Rigler, R.; Orrit, M.; Basche, T. *Single Molecule Spectroscopy*; Springer-Verlag: Berlin, 2001.
2. (a) Bonnell, D. *Scanning Probe Microscopy and Spectroscopy Theory, Techniques, and Applications*, 2nd Ed.; Wiley-VCH: New York, 2001. (b) Moerner, W. E.; Orrit, M. *Science* **1999**, 283, 1670. (c) Gimzewski, J. K.; Joachim, C. *Science* **1999**, 283, 1683.
3. (a) Weiss, S. *Science* **1999**, 283, 1676. (b) Mehta, A. D.; Rief, M.; Spudich, J. A.; Smith, D. A.; Simmons, R. M. *Science* **1999**, 283, 1689.
4. (a) Paul, W. *Rev. Mod. Phys.* **1990**, 62, 531. (b) Arnold, S.; Folan, L. M. *Rev. Sci. Instrum.* **1986**, 57, 2250.
5. March, R. E.; Todd, J. F. J. *Practical Aspects of Ion Trap Mass Spectrometry, Vol. I, II*; CRC Press: New York, 1995.
6. Schlemmer, S.; Illemann, J.; Wellert, S.; Gerlich, D. *J. Appl. Phys.* **2001**, 90, 5410.
7. Winter, H.; Ortjohann, H. W. *Am. J. Phys.* **1991**, 59, 807.
8. The error of mass determination (± 0.0001) correspond to $+1\sigma$ (standard deviation) for 110 measurements on the same SiO₂ particle for this particular case. Similar error ranges were obtained for over 50 different SiO₂ particles with different mass.