Mass Concentration and Primary Particle Size of Metal Nanoparticle Agglomerates from Spark Discharge Measured by Universal NanoParticle Analyzer

Jing Wang[1,2] , Zhun Liu[3] , Seong Chan Kim[3] , and David Pui[3]

1 Institute of Environmental Engineering, ETH Zurich, Zurich, 8093, Switzerland
2 Empa, Analytical Chemistry, 8600 Dübendorf, Switzerland
3 Particle Technology Laboratory, University of Minnesota, 55414, USA

Introduction

Many nanomaterials are manufactured in the form of nanoparticle agglomerates, which are made up of clusters or chains of nanosize spheres referred to as primary particles. Combustion processes are used to manufacture a variety of materials in agglomerate form including fumed silica, titanium dioxide, and carbon black (Pratsinis 1998[1], Wang et al. 2011[2]). Diesel particulate and soot from building fires are also known to be in agglomerated form (Kim et al. 2009[3]). Agglomerates may possess complicated structures, which makes measurement a difficult task. One of the most common methods for agglomerate measurement is electron microscopy, which can provide direct measurement of the structural properties (Koylu et al. 1995[4], Rogak et al. 1993[5], Shin et al. 2009[6] among many others). However, taking electrical micrographs and performing image analysis can be time consuming and expensive. In addition, interpretation of the 2D images for 3D results may rely on assumptions and cause inaccuracy. Fast and online measurement for agglomerates is required in many scenarios including measuring fast changing agglomerates, quality control for material manufacturing, monitoring toxic air-borne agglomerates, etc. Most of the current aerosol instruments are designed for spherical particles. Therefore, there is a need for instruments capable of fast and online measurement of gas-borne nanoparticle agglomerates.

We have developed an instrument, Universal NanoParticle Analyzer (UNPA), for online measurement of gas-borne nanoparticle agglomerates (Wang et al. 2010[7], Shin et al. 2010[8]). It is based on combined measurement of electrical mobility and unipolar charging properties. The UNPA can provide morphology information of airborne nanoparticles, and determine the primary sphere size if the agglomerates are composed of primary spheres with a fractal dimension less than two (loose agglomerates). Operated under the scanning mode, the UNPA can provide the number, surface area and volume distributions of loose agglomerates in the range of 50 to several hundred nanometers in several minutes. We have used the UNPA to measure metal nanoparticle agglomerates and the results are described here.

UNPA utilizes Differential Mobility Analyzer (DMA), Condensation Particle Counter (CPC) and Nanoparticle Surface Area Monitor (NSAM) to characterize airborne nanoparticle morphology and measure the number, surface area and volume distributions of airborne nanoparticles. The key parameter measured is the UNPA sensitivity, which is defined as the current I (fA) measured by the NSAM divided by the number concentration N (#/cm3) measured by the CPC

$$S = I/N \text{ (fA cm3).} \tag{1}$$

Charging theories of Chang (1981[9]) for aerosol particles of arbitrary shape indicate that the geometric surface area and electrical capacitance of the particles are two important parameters to determine the mean charge of non-spherical particles. The electrical capacitance of agglomerates may be computed using a variational method proposed by Brown and Hemingway (1995[10]). The surface area of loose agglomerates may be calculated using a mobility analysis developed by Lall and Friedlander (2006[11]). Shin et al. (2010[8]) combined the above analyses to show that the electrical capacitance of loose agglomerates is larger than that of spherical particles with the same mobility, and loose agglomerates can gain more charges from unipolar charging.

The primary particle size plays an important role in determination of the surface area and electrical capacitance, thus the charges on agglomerates. The UNPA sensitivity is related to the primary particle diameter d_p. We found that the UNPA sensitivity can be correlated to the primary particle size through a power law relation (Wang et al. 2010[7])

$$S = c_2 \left(\frac{12\pi\lambda}{c^* d_p^2} \frac{d_m}{C_c} \right)^k c_1 (d_p)^h \tag{2}$$

where c^* is a constant regarding particle orientation, λ is the mean gas free path, c_1, c_2, k and h are constants which can be determined from the experimental data. Then the sensitivity data from the experiments can be fitted into (2) to determine the primary particle diameter d_p. Once the primary particle size is determined, surface area and volume of the agglomerates can be calculated.

Experimental Methods

Periodic spark discharge can vaporize electrode materials and the subsequent nucleation/ condensation leads to nanoparticle formation (Schwyn et al. 1988[12]). The metal nanoparticles in our study were generated by a Palas spark generator (Model GFG-1000). Its design and operating principle can be found in the paper of Helsper et al. (1993[13]). The following electrodes for the spark generator have been used: gold (ESPI Metals, 0.125″ diameter, 99.999%), silver (ESPI Metals, 0.125″ diameter, 99.999%) and nickel (ESPI Metals, 0.125″ diameter, 99.995%). The generated nanoparticle agglomerates were neutralized and sampled by the UNPA.

Results and Discussion

For the metal nanoparticle agglomerates from the spark discharge generator, we determined the primary particle sizes for agglomerates using the sensitivity data and equation (2). We also analyzed electron micrographs and obtained the primary particle sizes. A comparison of the primary particle sizes from the two methods is shown in Table 2. It can be seen that the agreement for the primary particle size is good and UNPA can measure primary particles in a rather wide size range.

Table 1. Comparison of primary particle sizes measured by UNPA with those by TEM.

Particle	d_p, nm (UNPA)	d_p, nm (TEM)
Au	6.0	7.9 ± 1.5
Ag	8.4	11.8 ± 3.2
Ni	4.1	6.6 ± 1.0

SUMMARY

Nanoparticle agglomerates possess different electrical charging properties than spherical particles, which is the basis of our instrument UNPA. UNPA can measure the primary particle size in open-structured agglomerates and compute the number, surface area and volume distributions. UNPA measurement results for metal nanoparticles agglomerates agreed well with offline measurements.

REFERENCES

[1] Pratsinis, S. E. (1998). Prog. Energy Combust. Sci. 24:197-219.
[2] Wang, J., Asbach, C., Fissan, H., Hülser, T., Kuhlbusch, T.A.J., Thompson, D. and Pui, D.Y.H. (2011), *In press, J. Nanoparticle Research*, DOI 10.1007/s11051-011-0236-z.
[3] Kim, S. C., Wang, J., Emery, M. S., Shin, W. G., Mulholland, G. W., and Pui, D. Y. H. (2009). *Aerosol Sci. & Technol.* 43:344-355.
[4] Koylu, U. O., Faeth, G. M., Farias, T. L., and Carvalho, M. G. (1995). *Combust. Flame.* 100:621-633.
[5] Rogak S.N., Flagan R.C., Nguyen H.V. (1993) *Aerosol Sci Technol* 18:25-47.
[6] Shin, W-G, Wang, J., Mertler, M., Sachweh, B., Fissan, H., Pui, D.Y.H. (2009) *J. Nanoparticle Research.* 11, 163 – 173.
[7] Wang, J., Shin, W. G., Mertler, M., Sachweh, B., Fissan, H., and Pui, D. Y. H. (2010). Aerosol Sci. & Technol. 44:97-108.
[8] Shin, W. G., Wang, J., Mertler, M., Sachweh, B., Fissan, H., and Pui, D. Y. H. (2010) J. Aerosol Sci. 41:975-986.
[9] Chang, J. S. (1981). J. Aerosol Sci. 12:19-26.
[10] Brown, R. C., and Hemingway, M. A. (1995). *J. Aerosol Sci.* 26 (8):1197-1206.
[11] Lall A.A., Friedlander S.K. (2006) *J. Aerosol Sci* 37: 260-271.
[12] Schwyn, S., Garwin, E., and Schmidt-Ott, A. (1988). *J. Aerosol Sci.* 19 (5):639-642.
[13] Helsper, C., Molter, W., Loffler, F., Wadenpohl, C., Kaufmann, S., and Wenninger, G. (1993). Atmospheric Environ. 27A (8):1271-1275.

Mass Concentration and Primary Particle Size of Metal Nanoparticle Agglomerates from Spark Discharge Measured by Universal NanoParticle Analyzer

University of Minnesota

ETH Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

EMPA Materials Science & Technology

Zhun Liu, Seong Chan Kim, David Y.H. Pui, Particle Technology Lab, University of Minnesota
Heinz Fissan, Institut für Energie- und Umwelttechnik eV (IUTA), Germany
Jing Wang, Empa, Swiss Federal Laboratories for Materials Testing and Research, and Institute of Enviromental Engineering, ETH Zurich

Overview

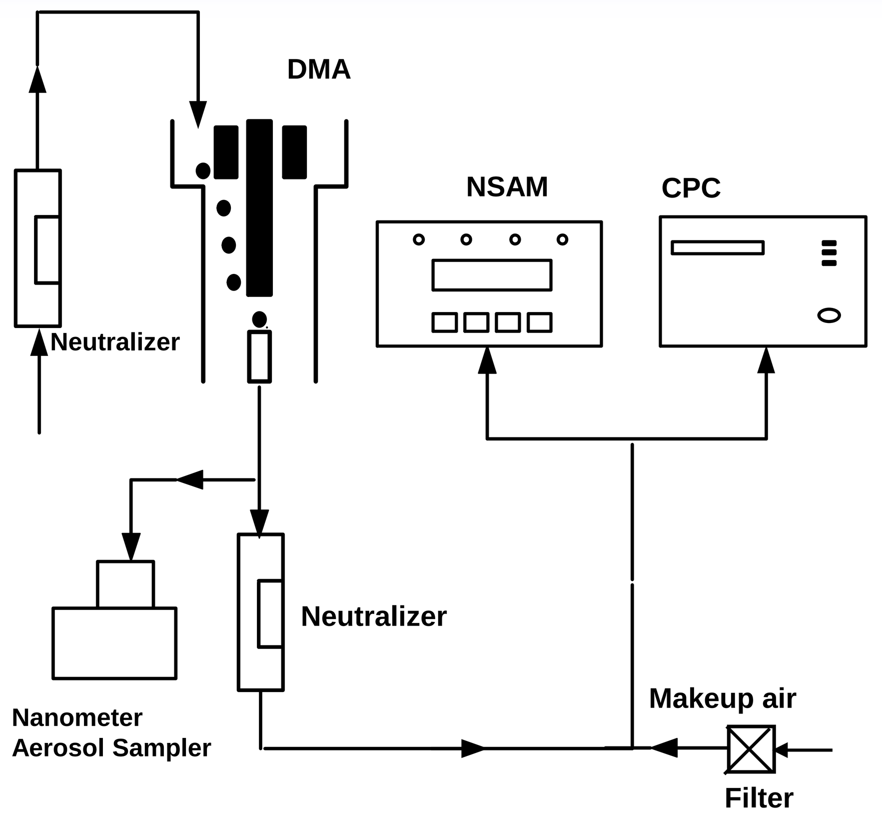
We describe here experiments in which a recently developed instrument called Universal NanoParticle Analyzer (UNPA) (Wang et al., 2010) was used in the measurement of metallic nanoparticle agglomerates generated from spark-discharge and coagulated inside an agglomeration chamber. The primary particle sizes were measured and the number, surface area, and volume distribution for loose agglomerates were obtained.

Background and Motivation

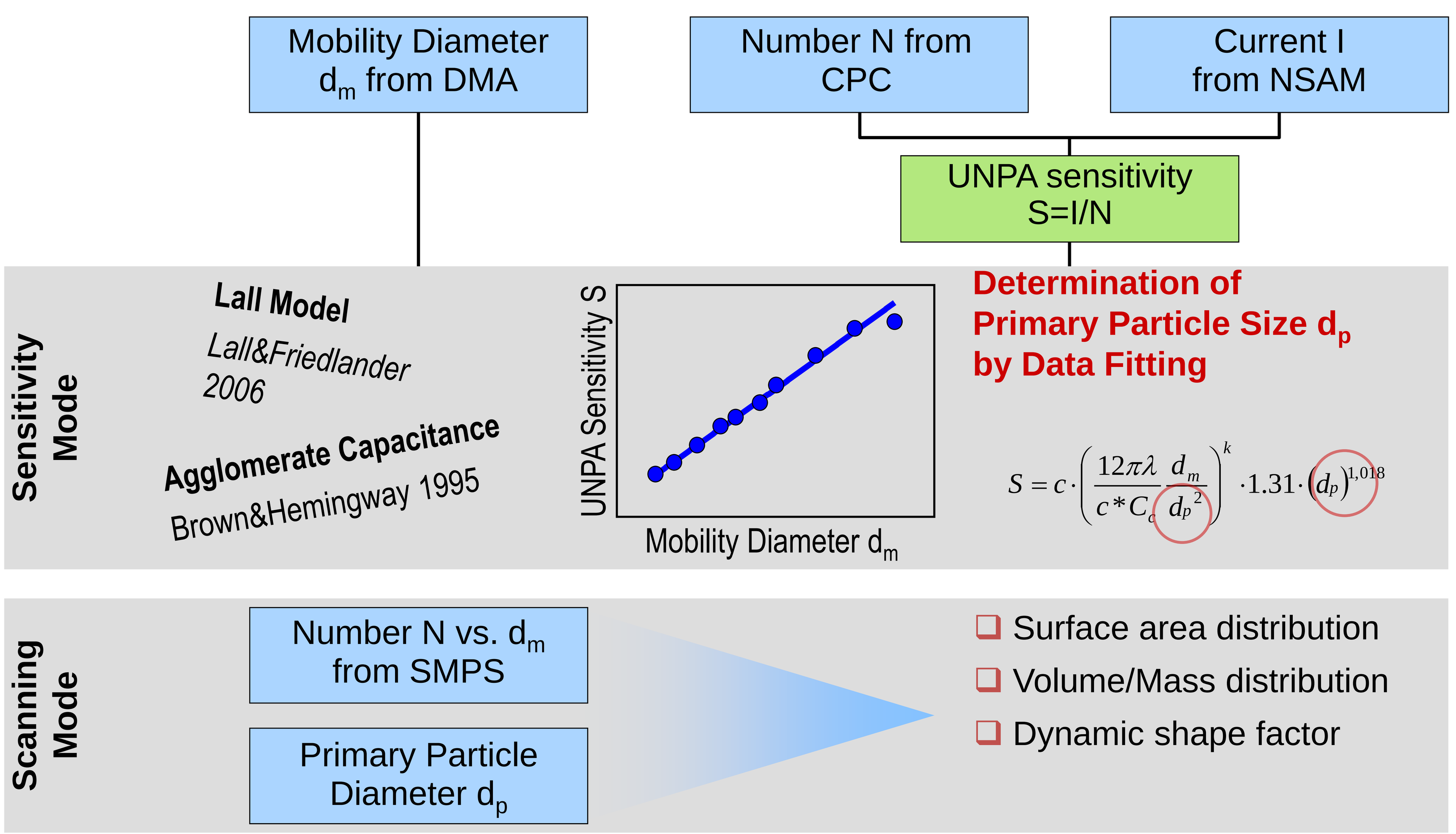
Nanoparticle agglomerate characterization and measurement is a popular area for recent aerosol research because most naturally occurring aerosols exist in agglomerate form rather than single spherical particle and many engineered aerosols (TiO_2, SiO_2) are agglomerates, because of the high concentration in the synthesis process. This is also a positive safety feature, because larger agglomerates are less mobile than single nanopartcle. We describe here experiments in which a recently developed instrument called Universal NanoParticle Analyzer (UNPA) (Wang et al., 2010) was used in the measurement of metallic nanoparticle agglomerates generated from spark-discharge and coagulated inside an agglomeration chamber.

Schematic of UNPA

- Modified SMPS-measuring technique for number distribution
- NSAM (a unipolar charger combined with an electrometer), provides information on charging properties
- Offline-sampler for SEM/TEM analysis
- SMPS + NSAM + New model allows for characterization of agglomerates (shape factor, primary particle size, volume, etc.)

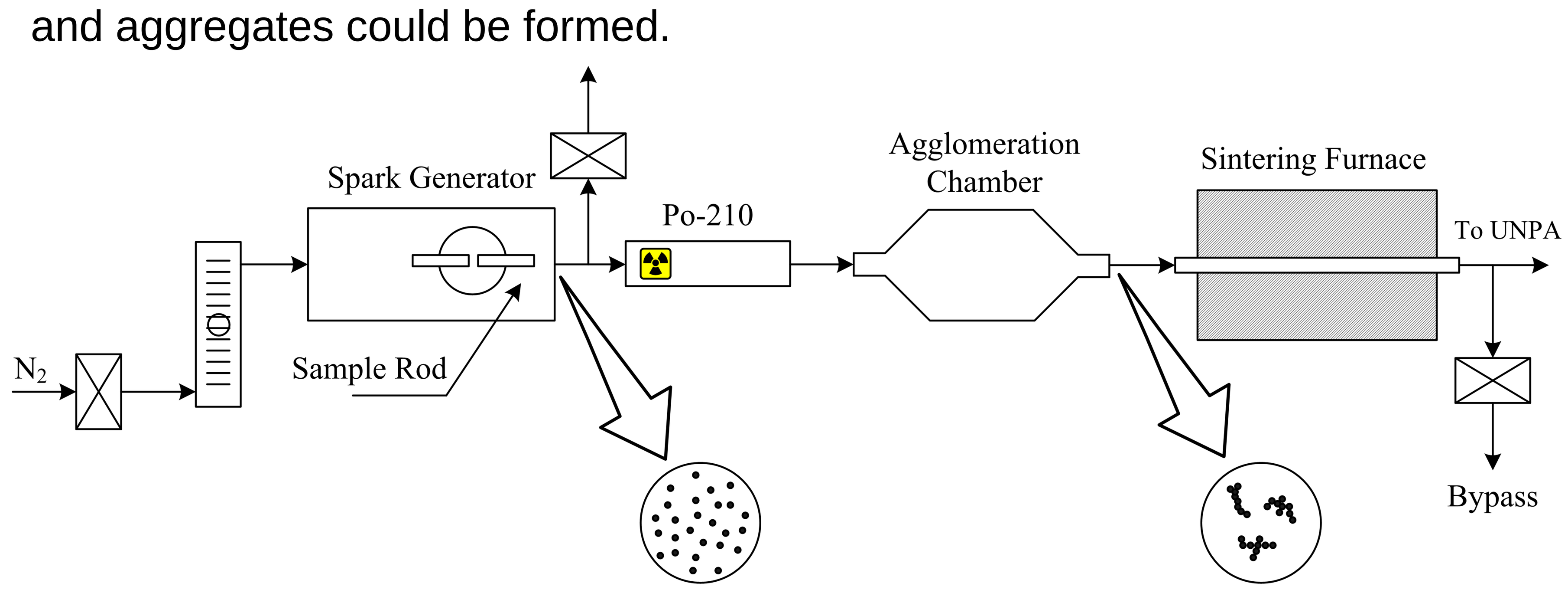


UNPA Operation



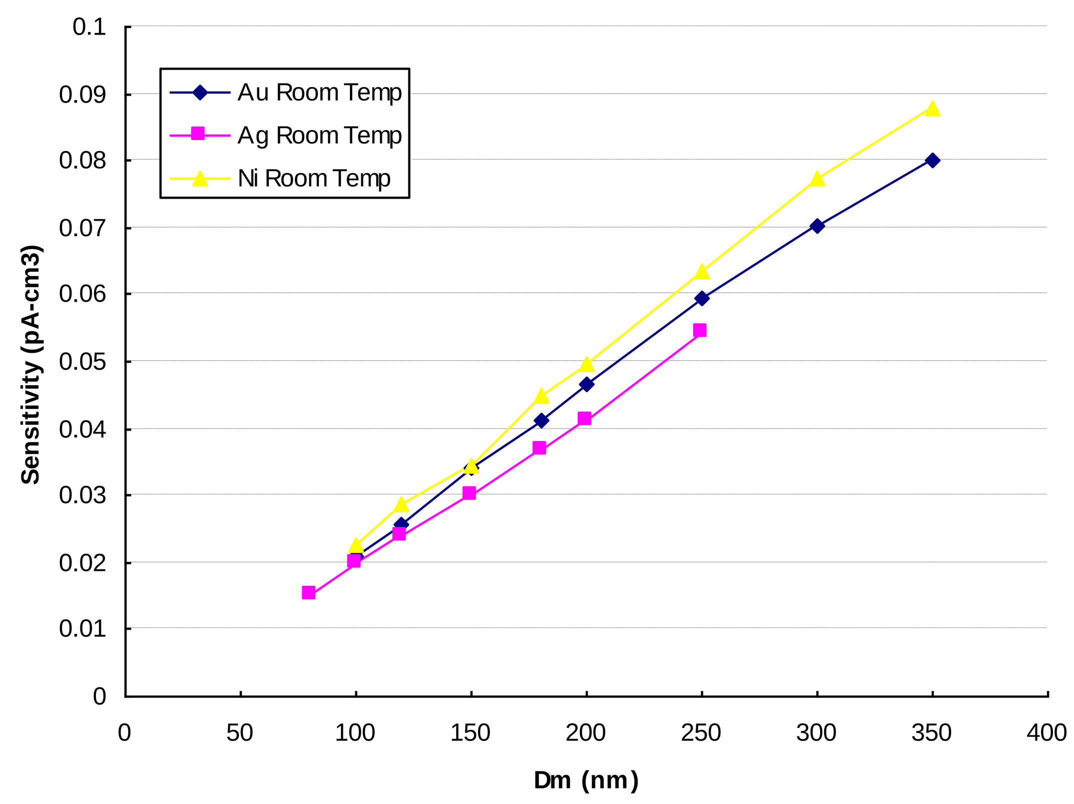
Experimental Setup

Nanoparticles of gold, silver and nickel were generated from a spark generator. They were then neutralized in a Po-210 bi-polar charger and sent to an agglomeration chamber, where they may coagulate and grow in size. Morphology control for the agglomerates was achieved by a sintering furnace and aggregates could be formed.



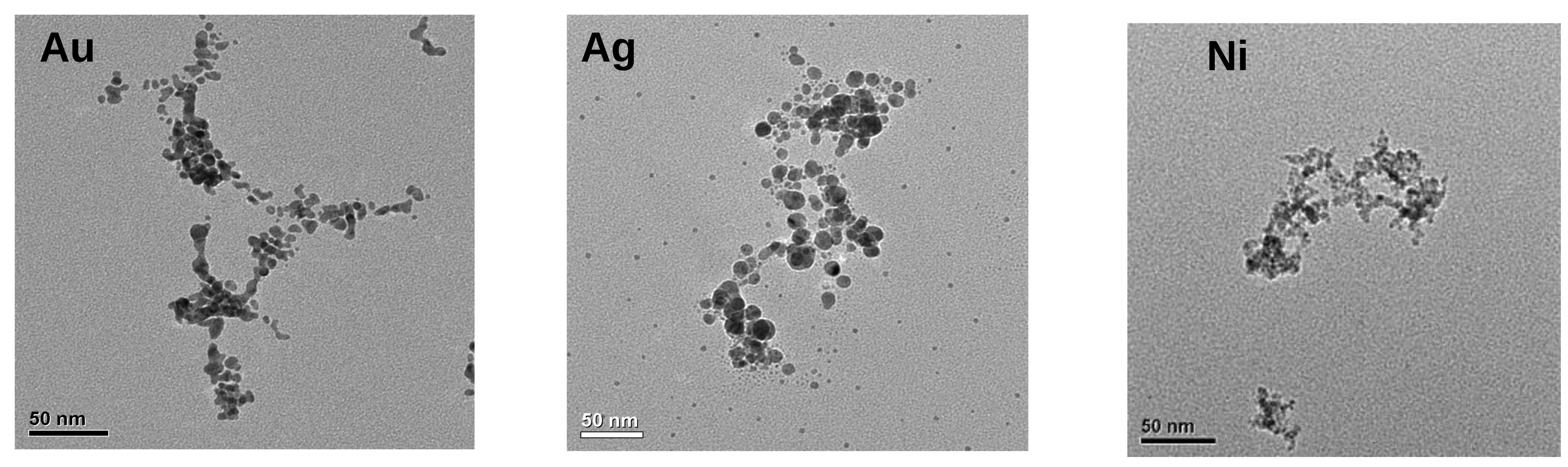
Results

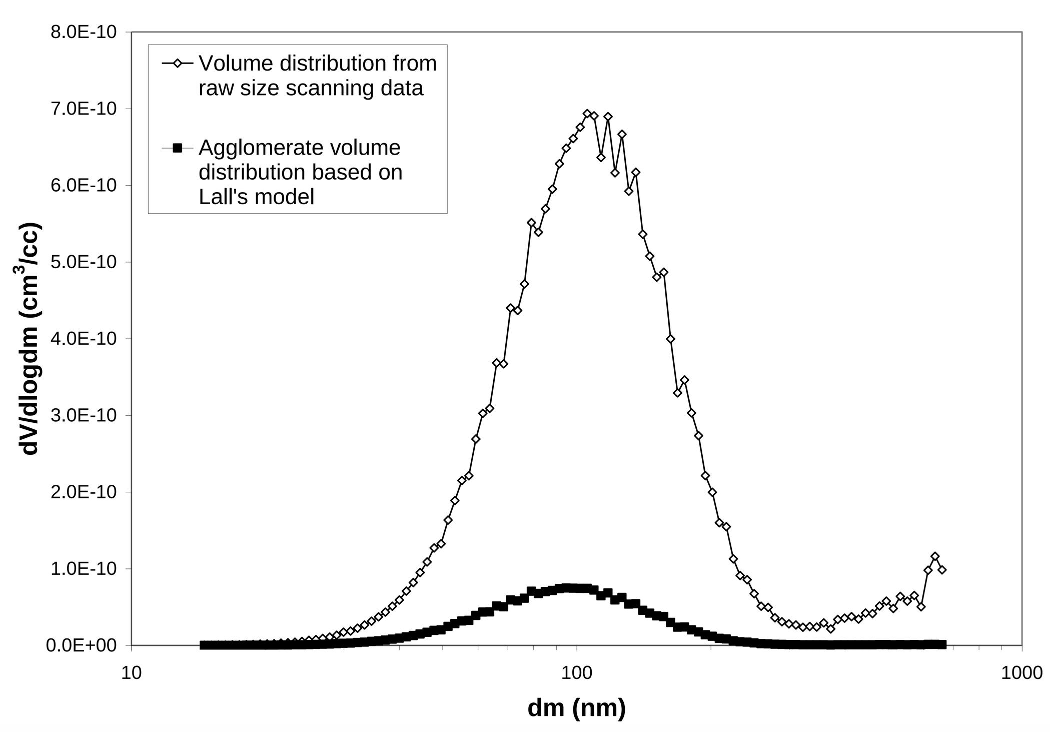
The UNPA sensitivity S, defined as $S = I/N$, where I is the current reading of NSAM internal electrometer and N is the concentration reading of CPC, was measured for agglomerates of Au, Ag, and Ni. It was used later to infer the primary particle size using methods described by Wang *et al.*, 2010.



The primary particle size d_p from UNPA is in good agreement with the value by electron microscopy (EM).

	d_p from UNPA (nm)	d_p from TEM (nm)	Standard deviation from TEM (nm)
Au agglomerate	5.97	7.90	1.47
Ag agglomerate	8.43	11.82	3.16
Ni Agglomerate	4.09	6.56	0.98





The value of d_p is used to correct the SMPS results and obtain number, surface area and volume distributions for loose agglomerates. The raw size scanning result assuming spheres overestimates the agglomerate volume concentration by about ten times.

Conclusions

- New UNPA measurement device facilitates extended characterization of nanoagglomerates, e.g. primary particle diameter, intrinsic parameters.
- Measurements for gold, silver and nickel nano-agglomerates genreated from a spark generator are in good agreement with offline-analysis.
- UNPA can significantly improve the measurement accuracy for loose agglomerates compared to instruments assuming spheres.

Publications related to UNPA

[1] Shin, Wang, Mertler, Sachweh, Fissan, and Pui, (2010) The Effect of Particle Morphology on Unipolar Diffusion Charging of Nanoparticle Agglomerates in the Transition Regime, accepted, J. Aerosol Sci.
[2] Wang, Shin, Mertler, Sachweh, Fissan, and Pui, (2010) Measurement of Nanoparticle Agglomerates by Combined Measurement of Electrical Mobility and Unipolar Charging Properties, Aerosol Science & Technology, 44, 97-108.
[3] Shin, Qi, Wang, Fissan, and Pui (2009), J. Aerosol Sci. 40, 463 – 468.
[4] Shin, Mulholland, Kim, Wang, Emery, and Pui, (2009) J. Aerosol Sci.40, 573-587.
[5] Shin, Wang, Mertler, Sachweh, Fissan, Pui, (2009), J. Nanoparticle Research. 11, 163 – 173.