Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Multi-element analysis of single nanoparticles by ICP-MS using quadrupole and time-of-flight technologies

Steffi Naasz[1], Stefan Weigel[1#], Olga Borovinskaya[2], Andrius Serva[3], Claudia Cascio[1$], Anna K. Undas[1], Felice C. Simeone[1&], Hans J. P. Marvin[1], Ruud J. B. Peters[1*].

[1] RIKILT – Wageningen UR, Akkermaalsbos 2, 6708 WB Wageningen, The Netherlands

[2] Tofwerk AG, Uttigenstrasse 22, CH-3600 Thun, Switzerland

[3] Fluidigm Corp., 7000 Shoreline Court, South San Francisco, CA 94080, USA

[#] current address: BfR – Federal Institute for Risk assessment, Max-Dohrn-Strasse 8-10, 10589 Berlin, Germany

[$] current address: EFSA - European Food Safety Authority, Via Carlo Magno, 1A, 43126 Parma PR, Italy

[&] current address: ISTEC – Institute of Science and Technology of Ceramic Materials, Via Granarolo 64-48018 Faenza, Italy

* Corresponding author: ruudj.peters@wur.nl

Table of contents

1. Materials and Methods

1.1 Selection of instruments

Table S1: Technical parameters of the ICP-TOFMS and ICP-QMS instruments tested in this study (referring to instrument manufacturer information).

	***icp*TOF**	**CyTOF® 2**	**Nexion® 350D**	**iCAP™ Q**
Detector	TOFMS	TOFMS	QMS	QMS
Type of detection for multiple elements	simultaneous	simultaneous	sequential	sequential
Detectable mass range	1 - 260 amu	89 - 209 amu	1 - 285 amu	2 - 290 amu
Data acquisition	33.000 mass spectra/sec	76.800 mass spectra/sec	100.000 points/sec	90.000 points/sec
Min. dwell time	30 µs	13 µs	100 µs	100 µs
Min. settling time	-	-	120 µs	75 µs

Table S2: Measurement parameters for icpTOF (Tofwerk AG, Switzerland).

Instrument parameter	**Conditions (all particles)**	**Conditions for measurements with H_2 (nano-steel platelets)**
Nebulizer Gas Flow (L min^{-1})	1.0	1.0
Auxiliary Gas Flow (L min^{-1})	0.8	0.8
CCT (H_2) Gas Flow (L min^{-1})	-	5
Spray chamber	quartz cyclonic	quartz cyclonic
Peristaltic Pump Speed (rpm)	40	40
Sample Flow Rate (mL min^{-1})	0.5	0.5
ICP RF Power (W)	1550	1550
Dwell time (triggered mode)	30 µs	30 µs
Ions attenuated	$^{40}Ar^+$, $^{35}Cl^+$, $^{32}O_2^+$, $^{16}O^+$	$^{32}O_2^+$
Isotopes monitored	^{48}Ti, ^{51}V, ^{52}Cr, ^{56}Fe, ^{58}Ni, ^{98}Mo, ^{107}Ag, ^{197}Au, ^{209}Bi	
Measured transport efficiency (%)	6-8	
Measured transmission efficiency	$4 \cdot 10^{-5}$	

Table S3: Measurement parameters for CyTOF® 2 (Fluidigm Corp.).

Instrument parameter	**Conditions (all particles)**
Nebulizer Gas Flow (L min^{-1})	0.14
Auxiliary Gas Flow (L min^{-1})	0.85
CCT (H_2) Gas Flow (L min^{-1})	not available
Spray chamber	quartz linear
Syringe drive injection	
Sample injection volume (µL)	500
Sample Flow Rate (mL min^{-1})	0.045
ICP RF Power (W)	1460
Dwell time (single element spICP-MS)	13 µs
Dwell time (multi-element spICP-MS)	13 µs

Elements monitored	^{107}Ag, ^{197}Au, ^{209}Bi
Measured transmission efficiency	$5\cdot10^{-5}$

Table S4: Measurement parameters for quadrupole ICP-MS Nexion® 350D (Perkin Elmer Scientific).

Instrument parameter	Conditions (all particles)	Conditions for measurements with He (nano-steel platelets)
Nebulizer Gas Flow (L min^{-1})	1.06	1.06
Auxiliary Gas Flow (L min^{-1})	1.20	1.20
CCT (He) Gas Flow (L min^{-1})	-	4.5
Spray chamber	quartz cyclonic	quartz cyclonic
Peristaltic Pump Speed (rpm)	40	40
Sample Flow Rate (mL min^{-1})	0.3	0.3
ICP RF Power (W)	1600	1600
Dwell time (single element spICP-MS)	3 ms	3 ms
Dwell time (multi-element spICP-MS)	100 µs	100 µs
Settling time	120 µs	120 µs
Isotopes monitored	^{47}Ti, ^{51}V, ^{52}Cr, ^{57}Fe, ^{60}Ni, ^{98}Mo, ^{107}Ag, ^{197}Au, ^{209}Bi	
Measured transport efficiency (%)	4-5	
Measured transmission efficiency	$5\cdot10^{-5}$	

Table S5: Measurement parameters for quadrupole ICP-MS iCAP™ Q (Themo Fisher Scientific).

Instrument parameter	Conditions (all particles)	Conditions for measurements with He (nano-steel platelets)
Nebulizer Gas Flow (L min^{-1})	1.12	1.12
Auxiliary Gas Flow (L min^{-1})	0.80	-
CCT (He) Gas Flow (L min^{-1})	-	1.0
Spray chamber	quartz cyclonic	
Peristaltic Pump Speed (rpm)	40	40
Sample Flow Rate (mL min^{-1})	0.3	0.3
ICP RF Power (W)	1550	1550
Dwell time (single element spICP-MS)	3 ms	3 ms
Dwell time (multi-element spICP-MS)	100 µs	100 µs
Settling time	75 µs	75 µs
Isotopes monitored	^{48}Ti, ^{51}V, ^{52}Cr, ^{56}Fe, ^{58}Ni, ^{98}Mo, ^{107}Ag, ^{197}Au, ^{209}Bi	
Measured transport efficiency (%)	6-8	
Measured transmission efficiency	$7\cdot10^{-5}$	

1.2 Materials

Table S6: Characteristics of nanoparticles composed of multiple elements.

Nanoparticle type	shape	Particle density (g $cm^{3\ -1}$)	Supplied primary particle size (nm)	Measured primary particle size (nm)	Particle number conc. (particles mL^{-1})	Conc. of stock suspension (mg L^{-1})
Au / Ag 60nm	spherical	-	61 ± 6 *	57 ± 5 #	2.2E+10	29

Au / Ag 80nm	spherical	-	79 ± 9 *	80 ± 5 #	6.4E+09	21
$BiVO_4$	amorph	7.0	-	69 ± 23 #	-	-
$(Bi_{0.5}Na_{0.5})TiO_3$	amorph	5.9	-	106 ± 49 #	-	-
Nano-steel (IRMM-383)	platelets	7.8	63 ± 47*	197 ± 89 #	8.0E+10 ≠	2 500

SEM
* TEM
≠ calculated considering the mass concentration and particle size of the prepared particle suspension

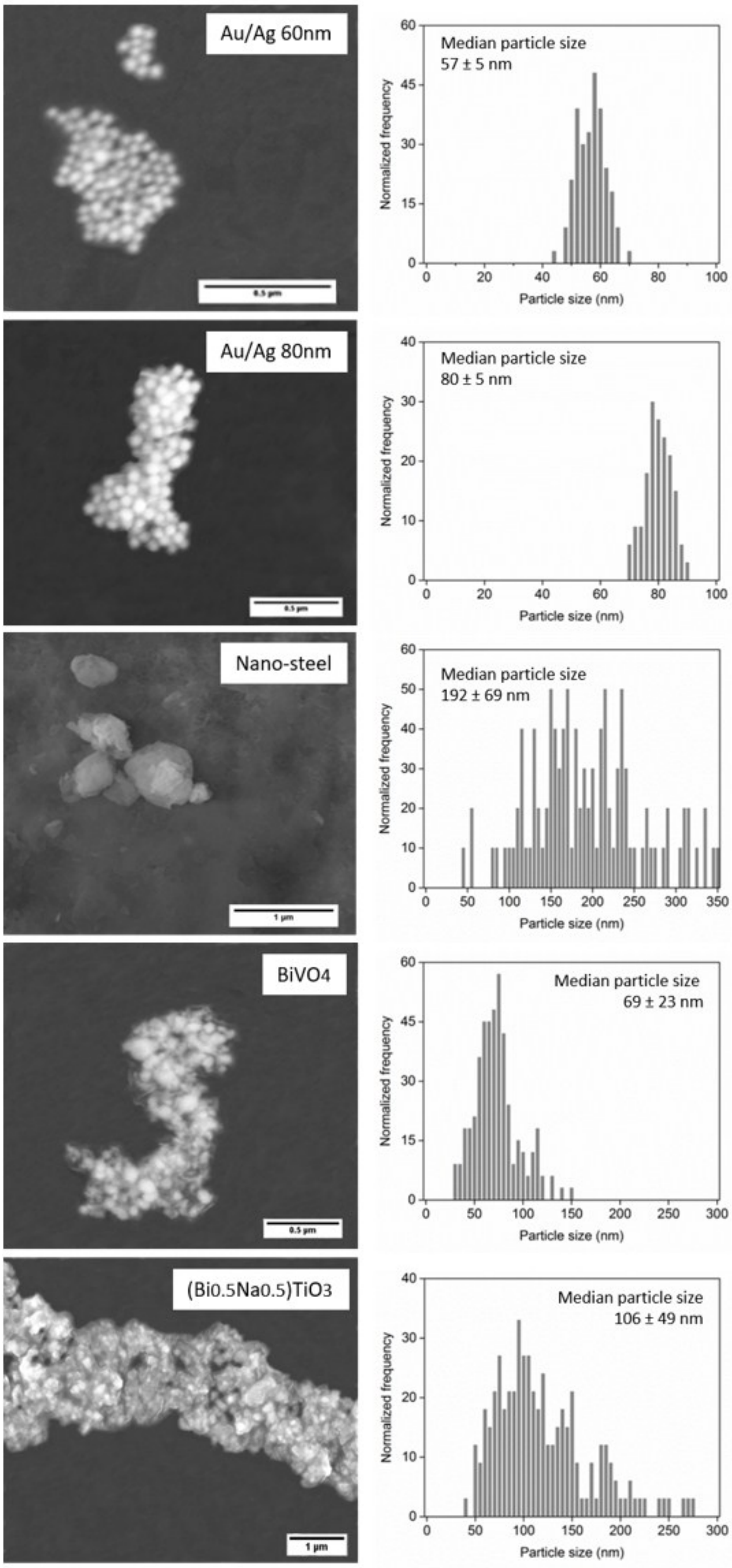

Figure S1: SEM images and primary particle size distribution of multi-element nanoparticles. Note that larger sized aggregates or agglomerates are present.

2. RESULTS

Fig. S2: Particle size distributions of spICP-MS measurements of Au-core/Ag-shell 60 nm material mentioned in table 1

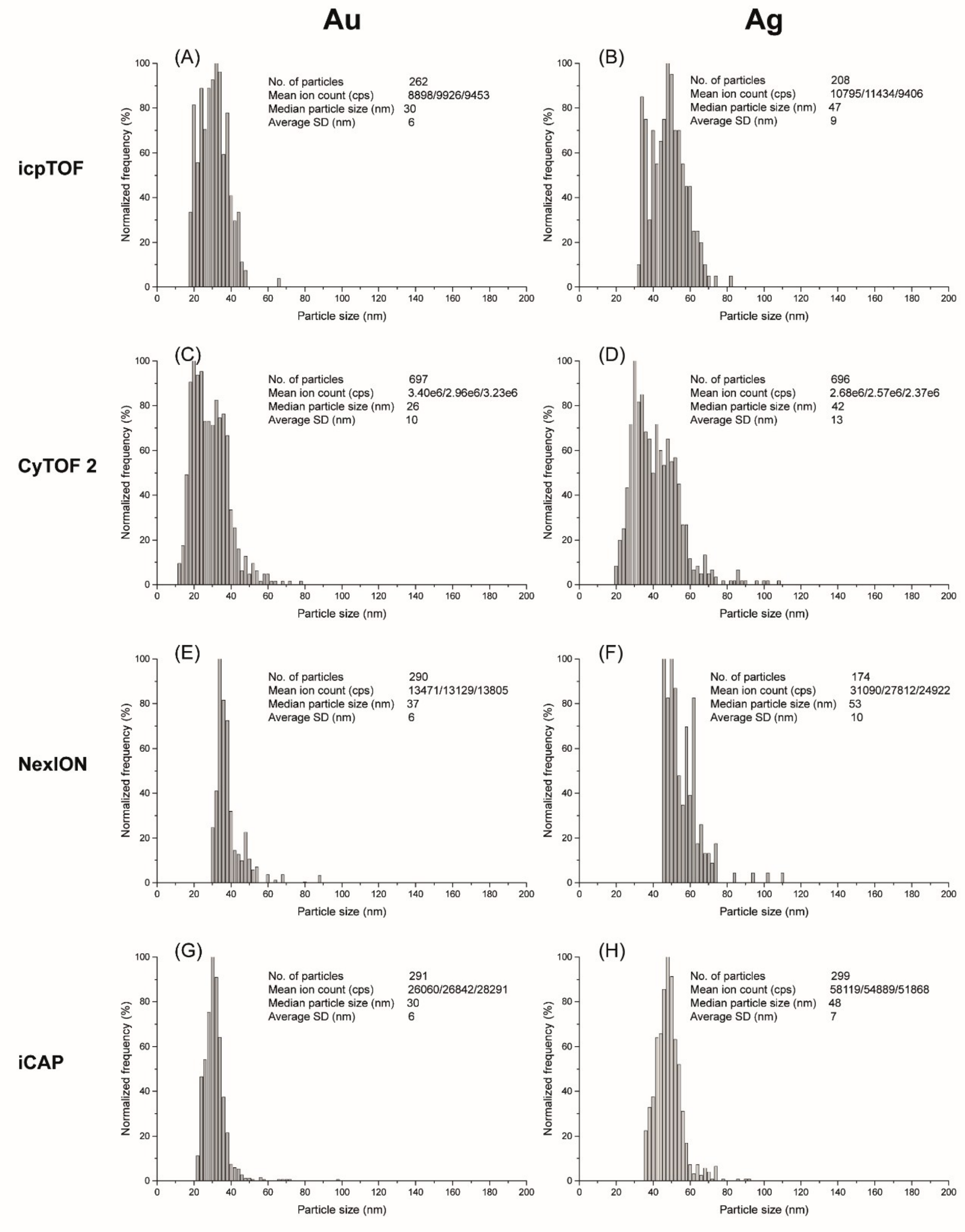

Fig. S2 (continued): Particle size distributions of spICP-MS measurements of Au-core/Ag-shell 80 nm material mentioned in table 1

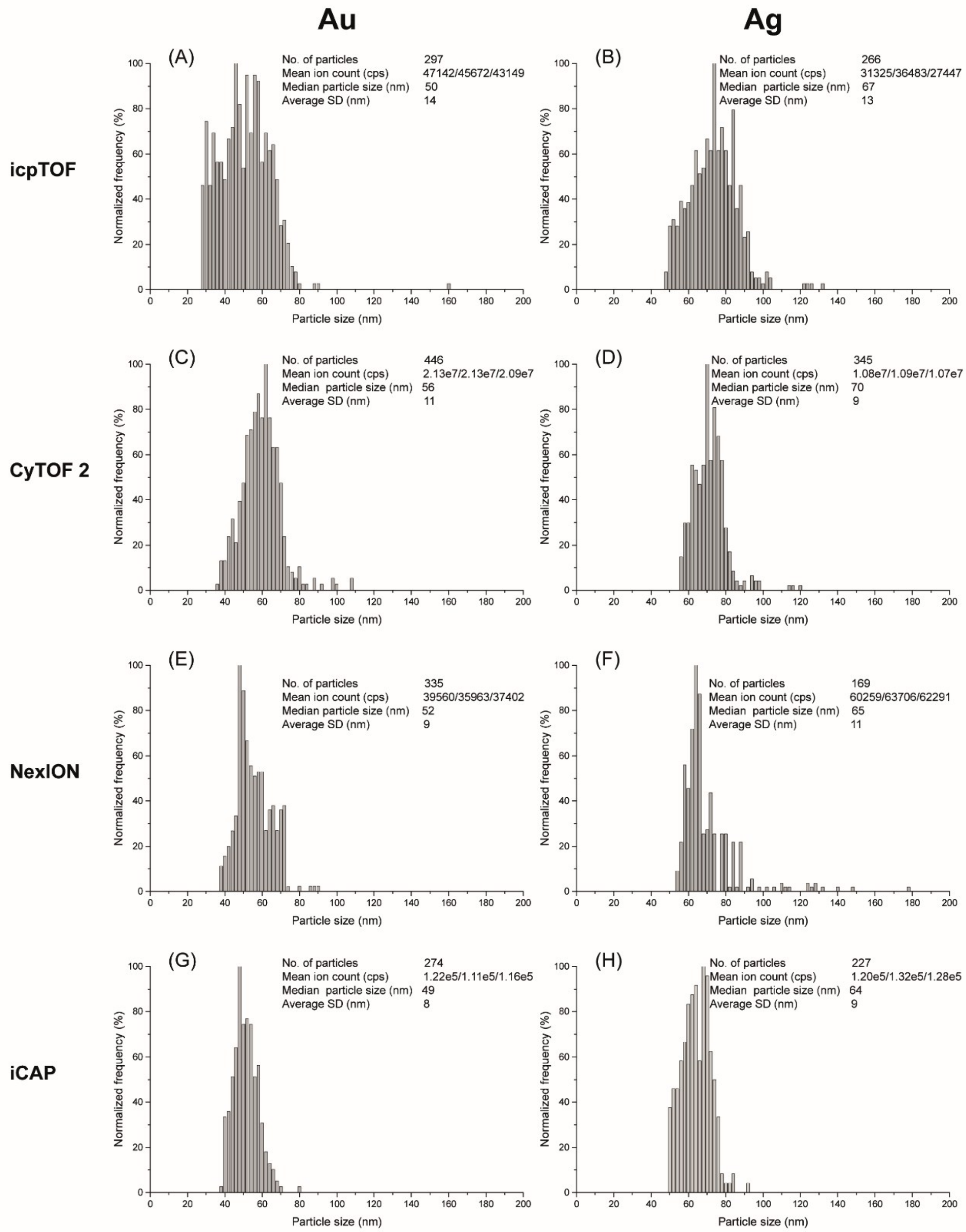

Fig. 2 (continued): Particle size distributions of spICP-MS measurements of $(Bi_{0.5}Na_{0.5})TiO_3$ and $BiVO_4$ materials mentioned in table 1

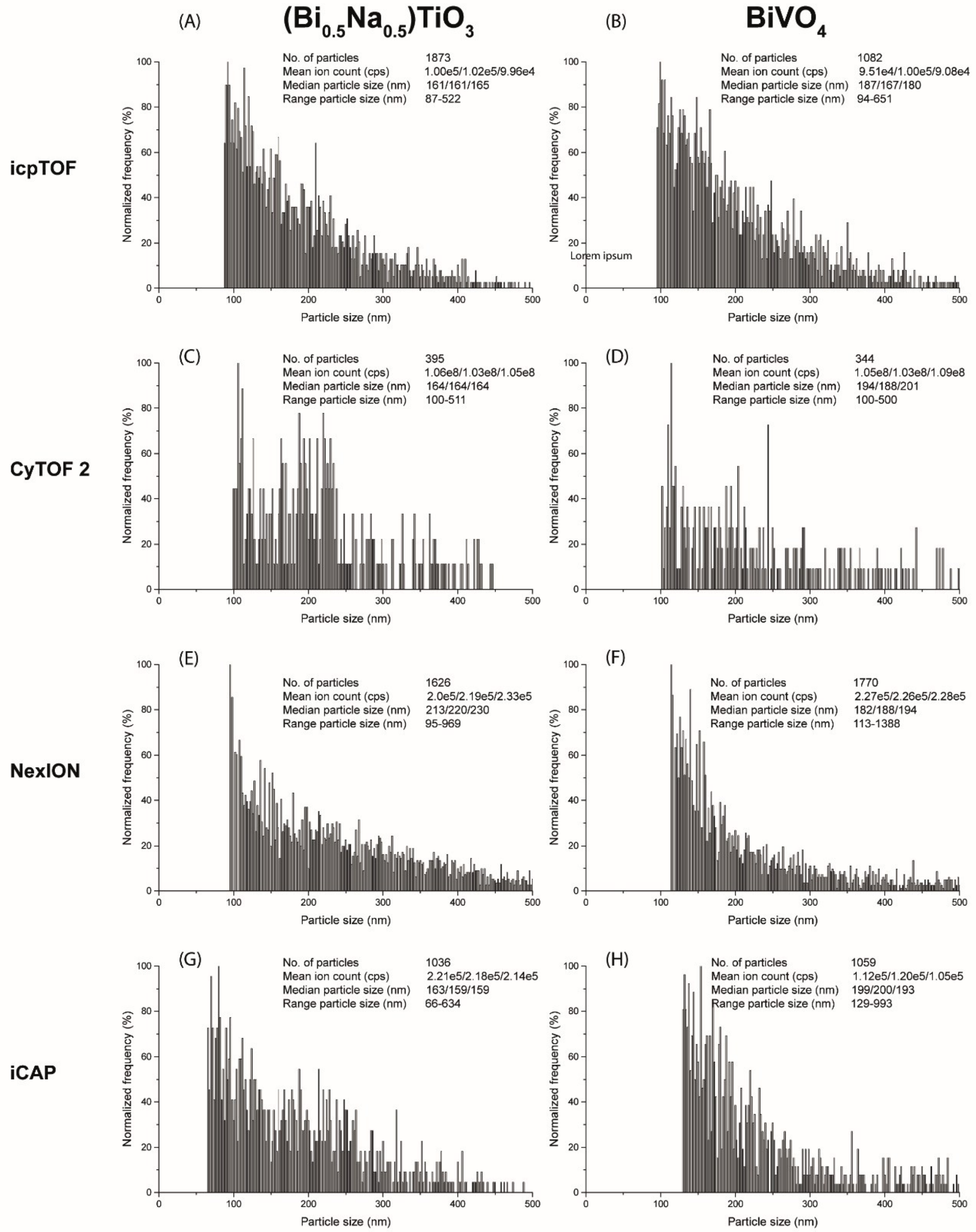

Fig. 2 (continued): Particle size distributions of spICP-MS measurements of nano-steel material mentioned in table 1

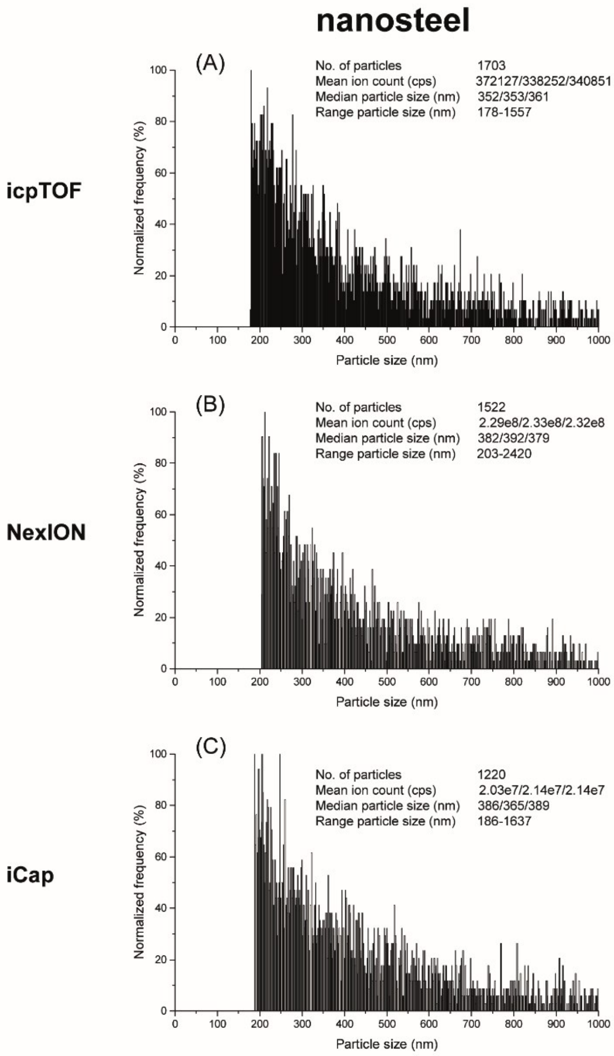

Fig. S3: Example of temporal shifts of Ti and Bi signals measured by icpTOF in single $(Bi_{0.5}Na_{0.5})TiO_3$ particles. (A) example of a large shift of 200 µs, (B) and small shift of 10-20 µs.

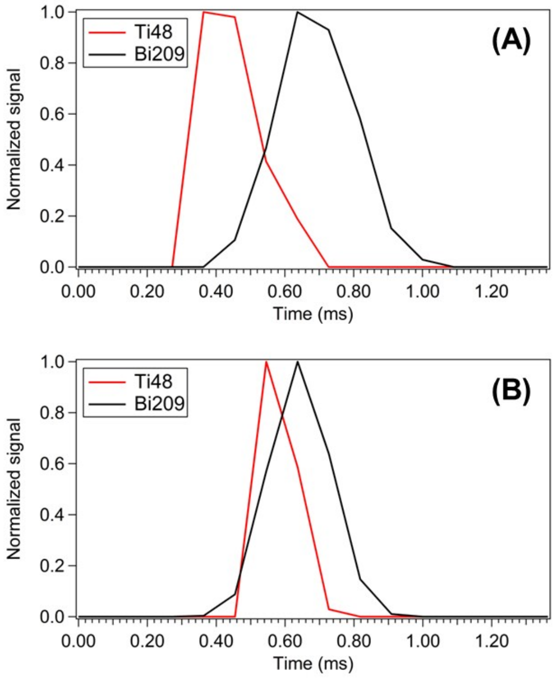

Fig. S4: Distribution histogram of V/Bi molar ratios in individual $BiVO_4$ NPs (a) and of Ti/Bi molar ratios in individual $(Bi_{0.5}Na_{0.5})TiO_3$ NPs measured by icpTOF. Only particles with signals of both elements above LOD were considered for molar ratio calculation.