Characterizations of inorganic NPs

Focus on naked NPs

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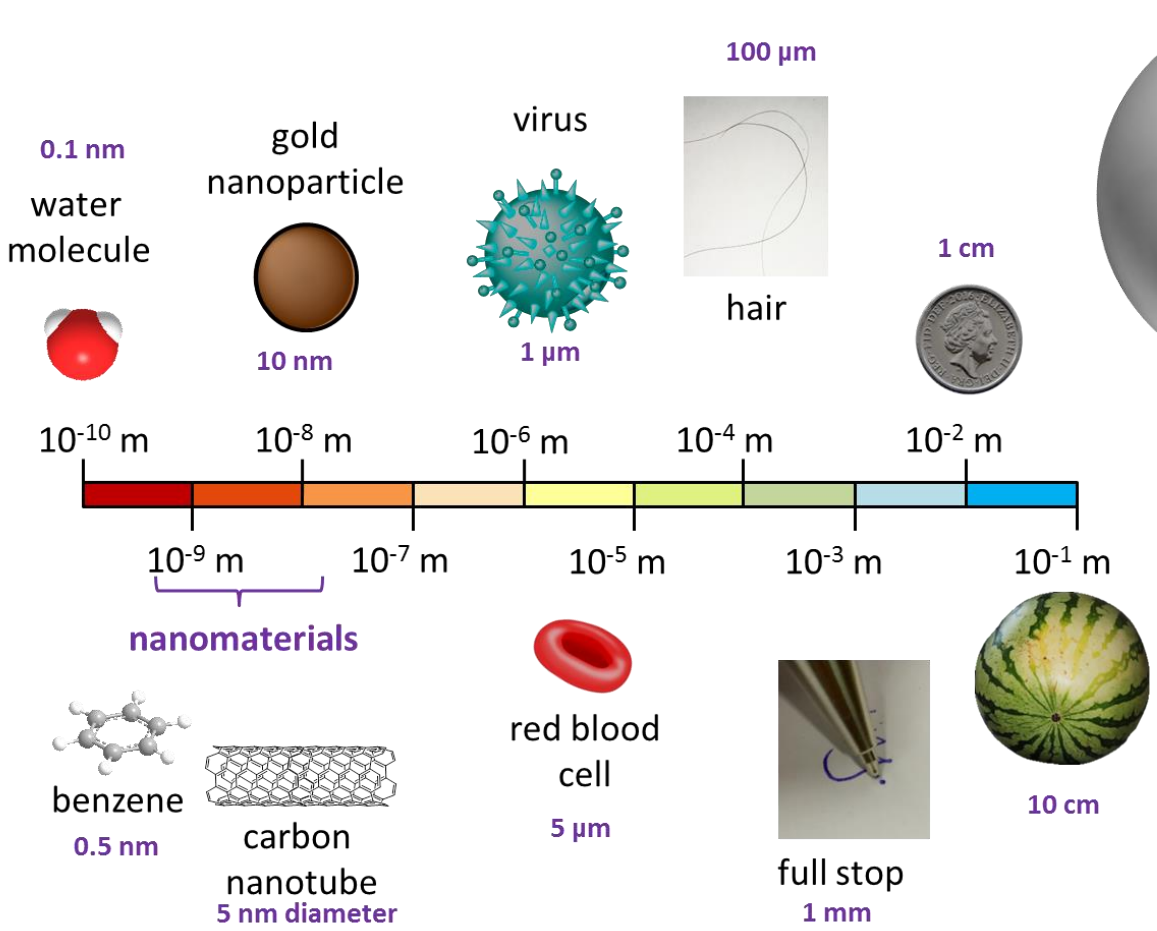
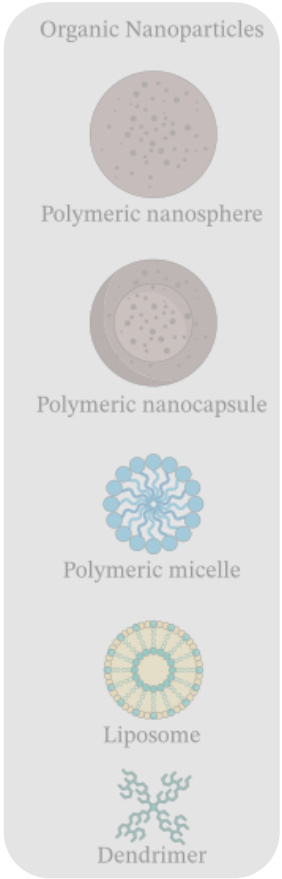
Nanoparticles

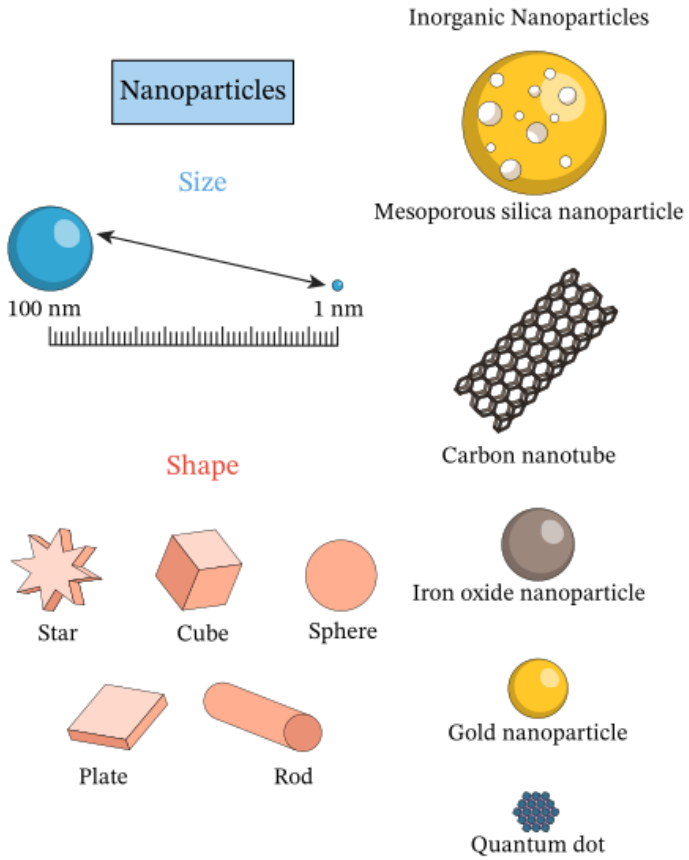
- Nanoparticle definition:
  - 3 dimensions between 1-100 nm
- High surface / volume ratio → Surface / interface crucial for applications

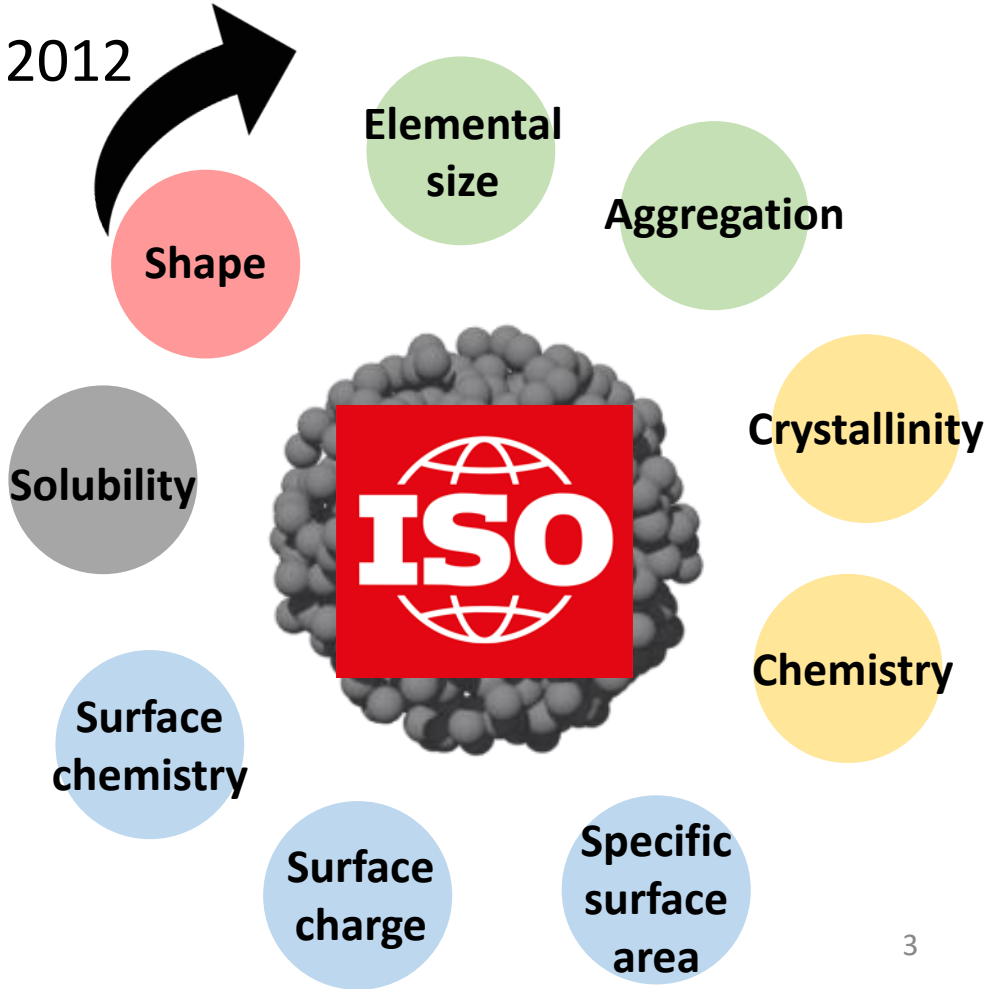


Nanoparticles

- Nanoparticle definition:
  - 3 dimensions between 1-100 nm
- High surface / volume ratio → Surface / interface crucial for applications
- Various parameters to study → ISO/TR 13014 :2012







Nanoparticles for biology

Functionalization for biomedical applications

Stabilization in physiological media
Surface modification

NP core

Specific properties

Biocompatible molecules – polymers…

Radioelement – Drug – Antibody – Protein …

Therapy

Diagnosis

Biocirculation?

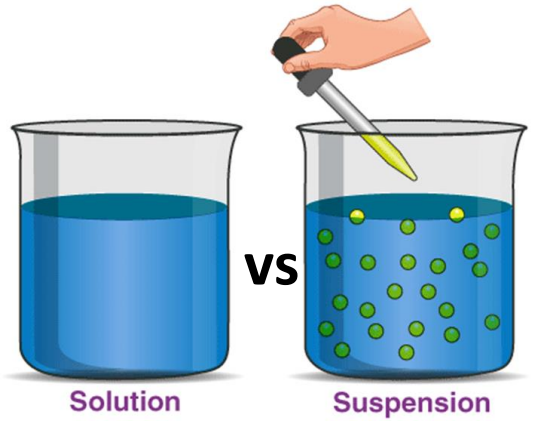
Biodistribution?

Toxicity?

Cellular uptake?

Terminology for this lecture

- For inorganic NPs: we talk about suspension not solution!

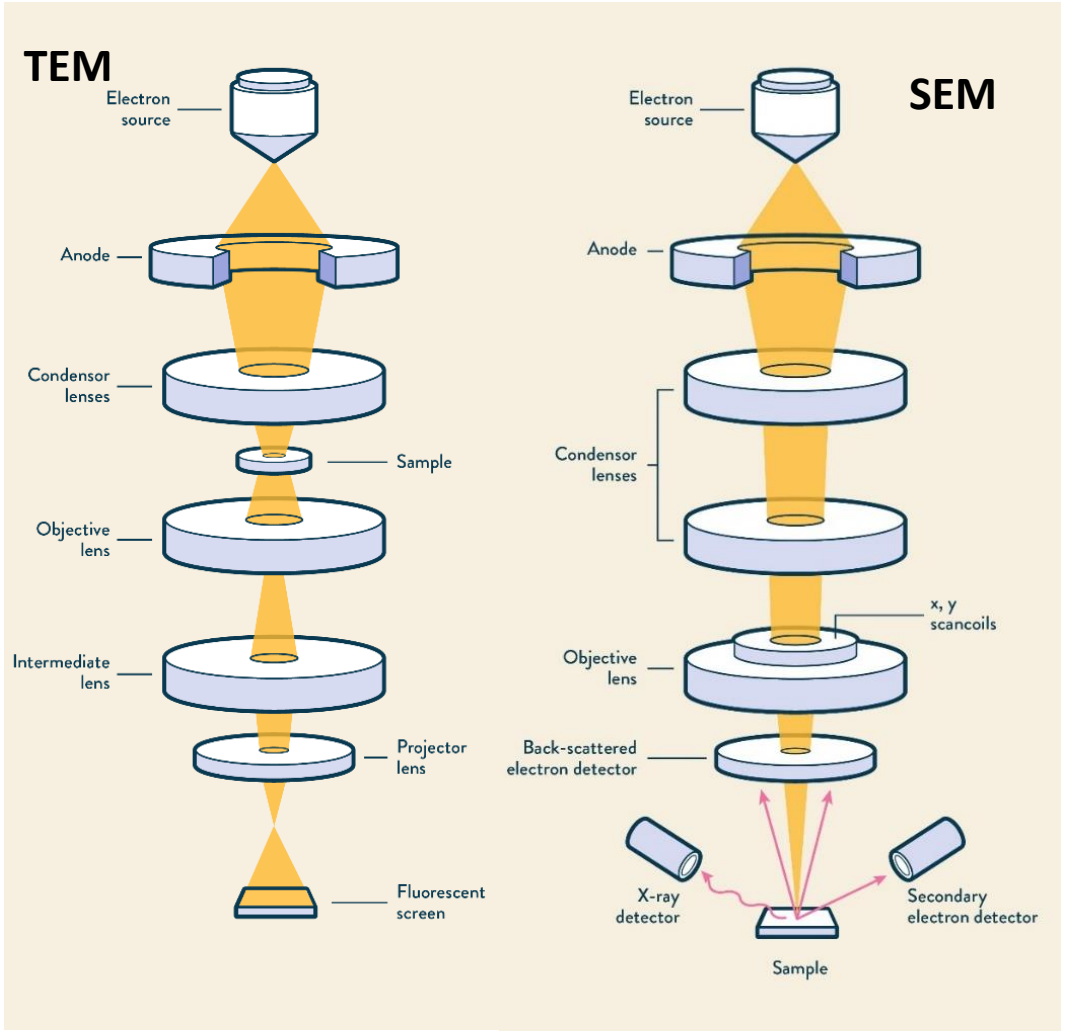


- Characterizations techniques are grouped and focused per ISO parameter
  - Some techniques are used for several parameters
- Techniques are listed as exhaustively as possible:
  - Some pro and cons + sample preparation
- Focus on bare / naked NPs
  - Surface organic modification in next lecture
- From my point of view: NPs in biology shoud avoid powder form

Shape

Shape

- Electronic Microscopy
  - Transmission or Scanning with electrons
  - Dried droplet (TEM) or powder (+coatings?) (SEM)
  - Resolution:
    - SEM : 1-2 10^6 X
    - TEM: 50 10^6 X



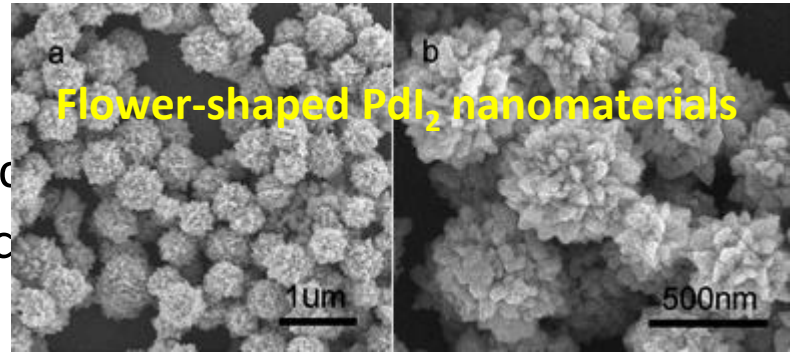
https://www.technologynetworks.com/analysis/articles/sem-vs-tem-331262

Shape

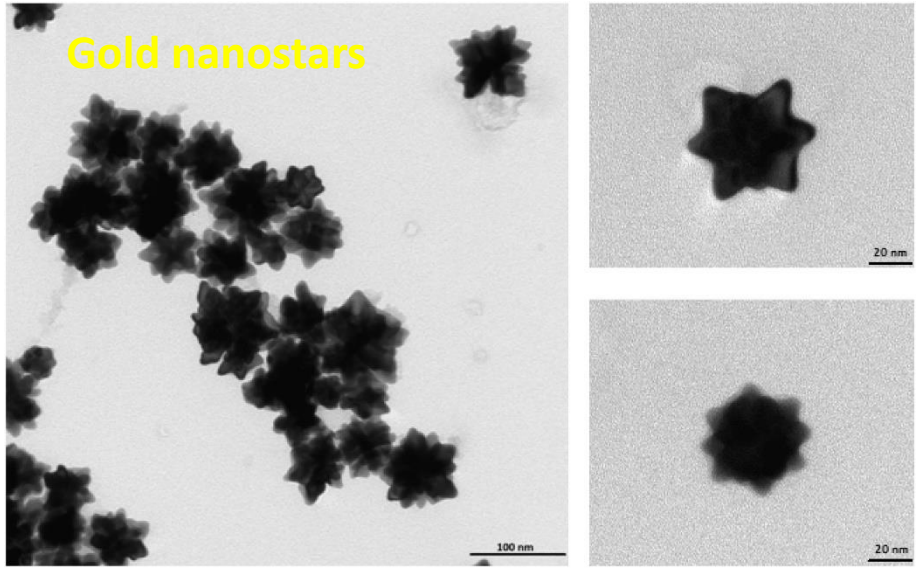
Shape

- Electronic Microscopy
  - Transmission or Scanning with elec
  - Dried droplet (TEM) or powder (+c
  - Resolution:
    - SEM : 1-2 10^6 X
    - TEM: 50 10^6 X

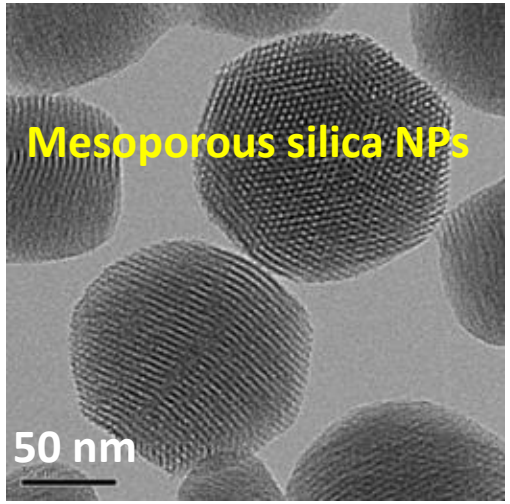
TEM /SEM	
Pros	**Cons**
Visual results	Dispersion
Low quantity	Significance?
Faster to use (SEM)	Only surface (SEM)
Cost less than TEM (SEM)	Need Coatings (SEM)



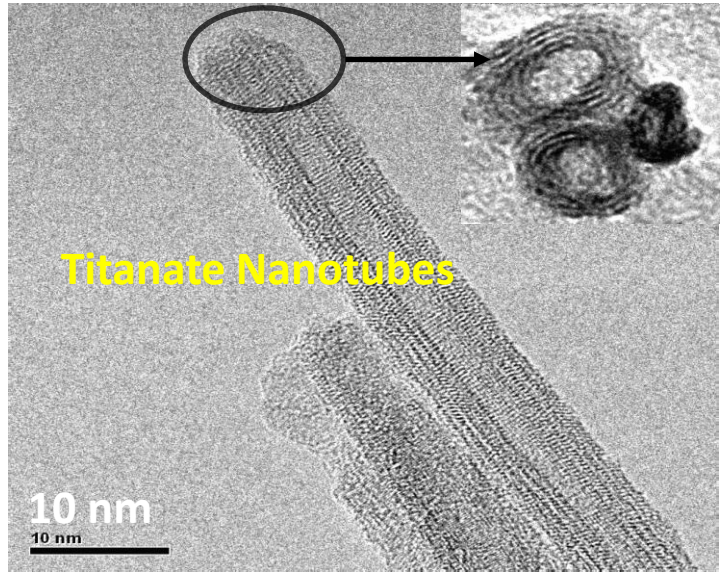
https://doi.org/10.1039/C0JM02610G



https://doi.org/10.1016/j.saa.2019.117469



https://doi.org/10.1016/j.jnoncrysol.2014.10.020

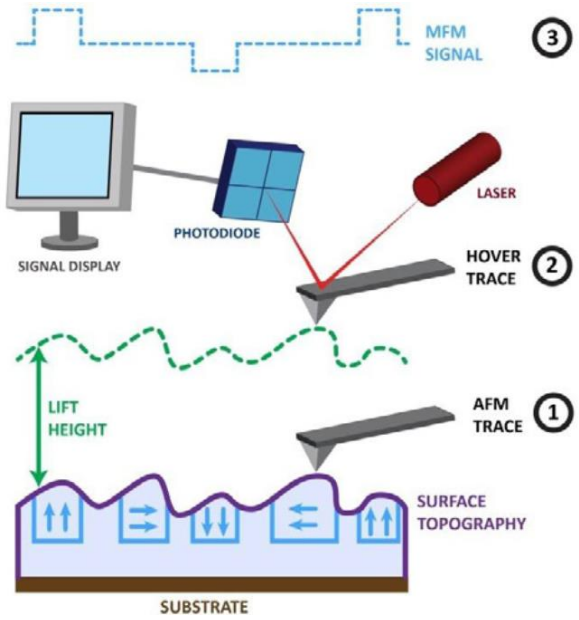


https://doi.org/10.1021/jp903195h

Shape

Shape

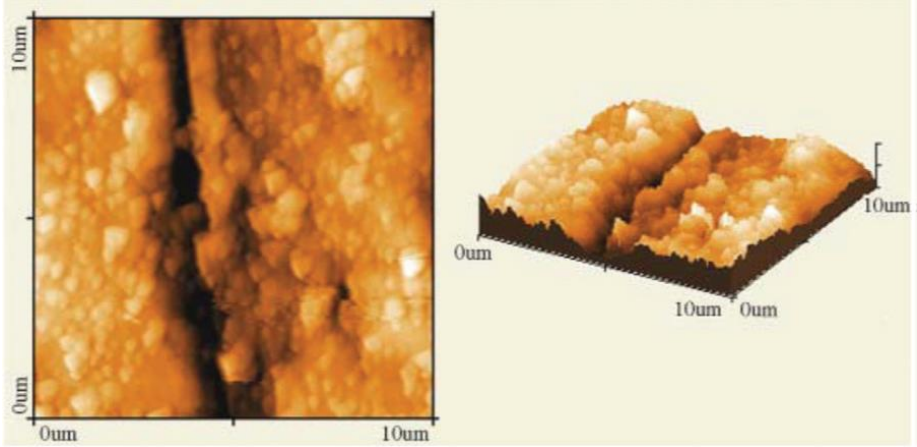
- Electronic Microscopy
- AFM Atomic Force Microscopy
  - Deposition of dried NPs on substrate
  - Maximal resolution 1 nm
    - AFM tip (diameter 5 nm) scans dried surface
    - Topographical trace recorded



AFM	
Pros	**Cons**
Higher resolution than SEM	Sample preparation
Smaller area than SEM (μm^3 vs mm^3)	

1) AFM tip scans sample surface to produce topographical trace
2) Cantilever is raised to a user-defined height away from the sample surface and the retrace follows the original topographical pattern from the first step
3) During retrace, magnetic signal scanned and recorded via reflection of laser beam off the back of cantilever and onto photodiode, where changes in cantilever deflection are detected

AFM images of a nickel plate with AgNPs



http://dx.doi.org/10.17756/nwj.2016-022

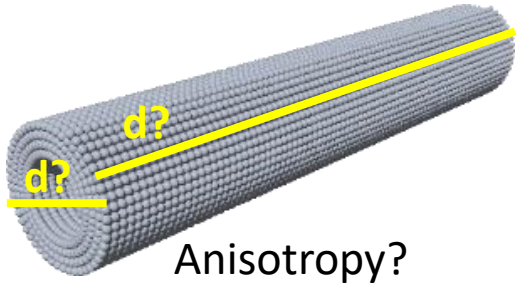
Size(S)

Shape

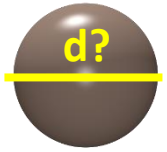
- **Size of NPs or SizeS of NPs?**

When asking about size of NPs the answer will depend on the topic:

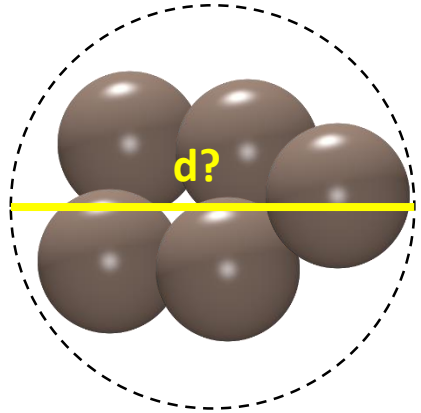
- Anisotropy
- Size of the single NP providing nanoproperties? (magnetism, plasmonic etc.)
  - Elemental size mainly dried: Microscopy, Atomic Force, X-Ray diffraction/diffusion, BET…
- Size of the NPs in suspension? (for biology)
  - Size of aggregates in liquid suspension: Light Diffusions, Sedimentation



Anisotropy?



Single NP



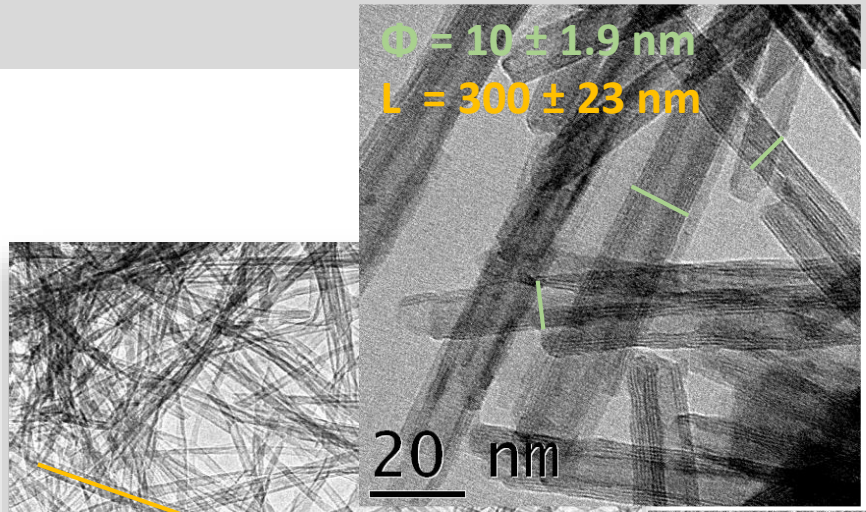
Agglomerate

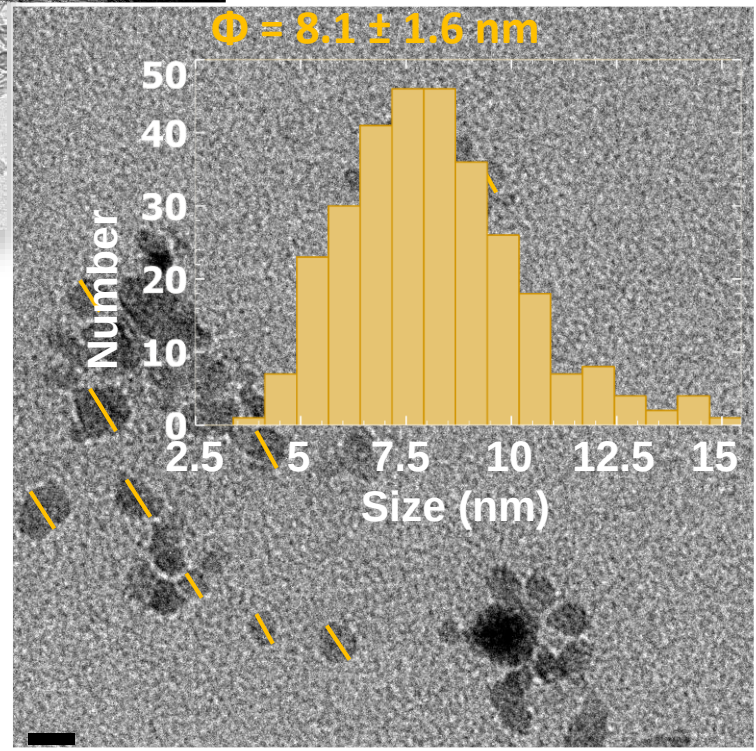
Size(S)

Shape **Size**

- Elemental size:
  - TEM, SEM
    - Anisotropy:
      - Shortest and biggest dimension?
      - Surface?
    - Significant number of NPs

    → Size distribution
      - ImageJ ?

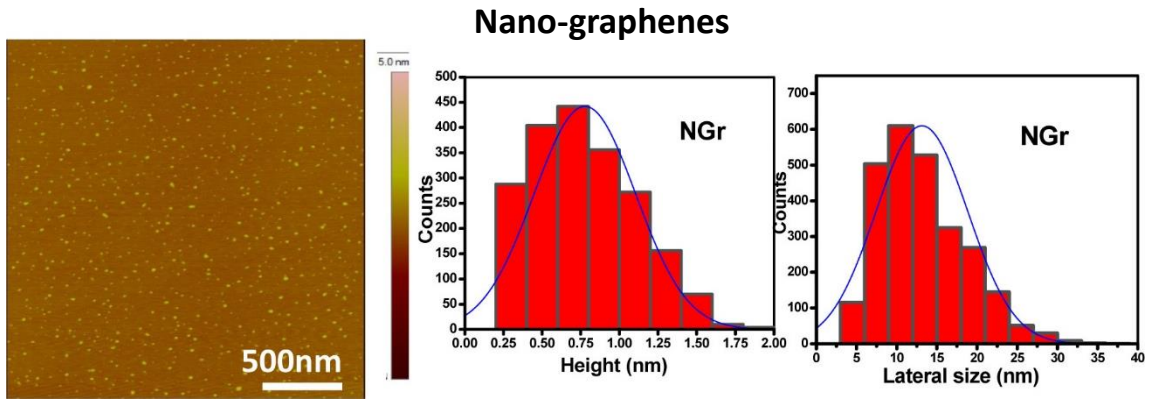




Size(S)

Shape **Size**

- Elemental size:
  - TEM, SEM
  - AFM
    - Size acquired with dedicated software



https://doi.org/10.1016/j.msec.2006.06.019

Size(S)

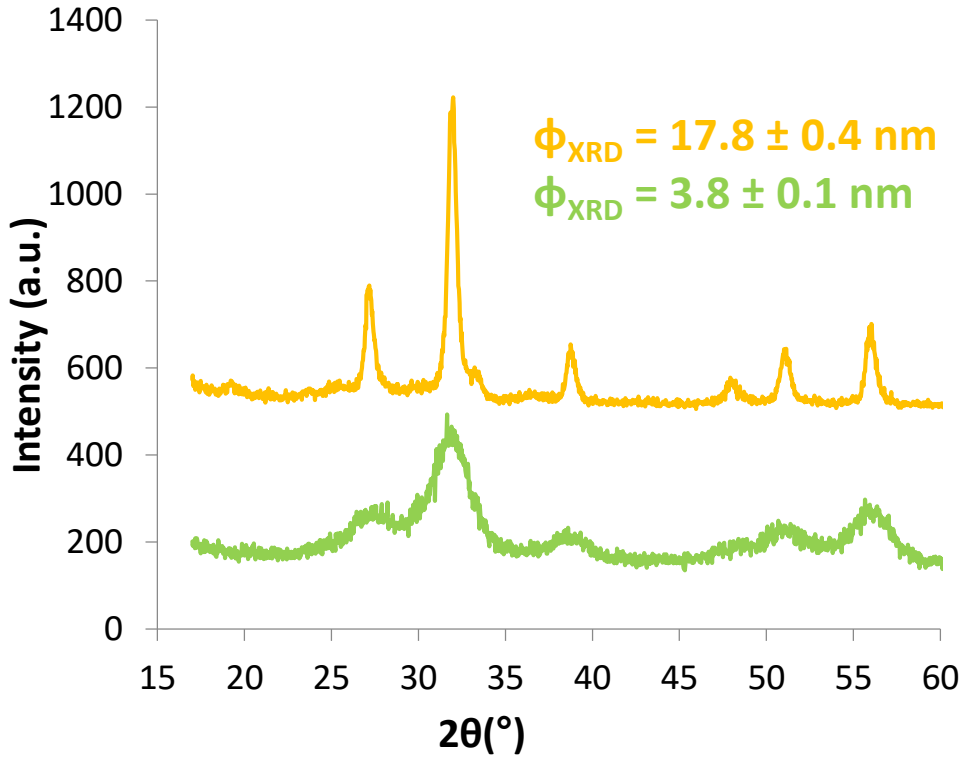
Shape | **Size**

- Elemental size:
  - TEM, SEM
  - AFM
  - XRD X-Ray Diffraction (details later)
    - Powder (>50 mg)
    - For monocrystalline NPs
    - Crystallite < 120 nm → broadening of diffraction peaks

Scherrer equation

$$\phi_{XRD} = \frac{K\lambda}{\beta cos\theta}$$

ϕ_{XRD} : mean size of the crystalline domain (≤ grain size)
K : shape factor close to 1
λ : Wavelength of X-Ray
β : Full width at half maximum in radian
cos θ : Cosine of Bragg angle (in radian)

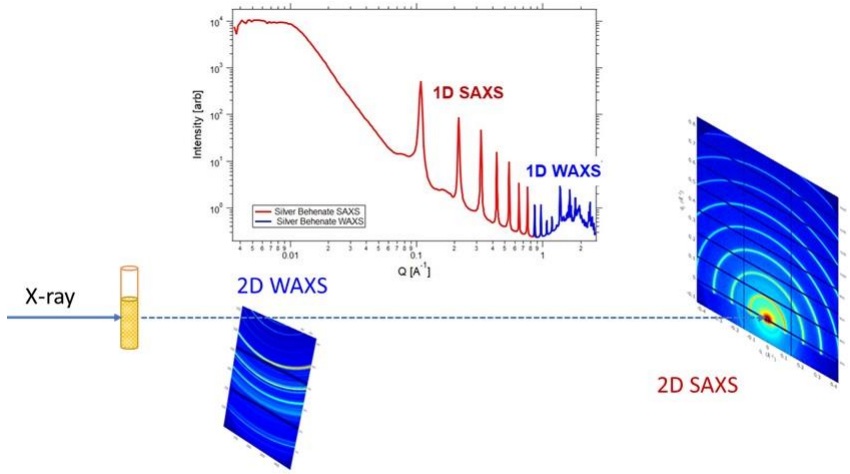


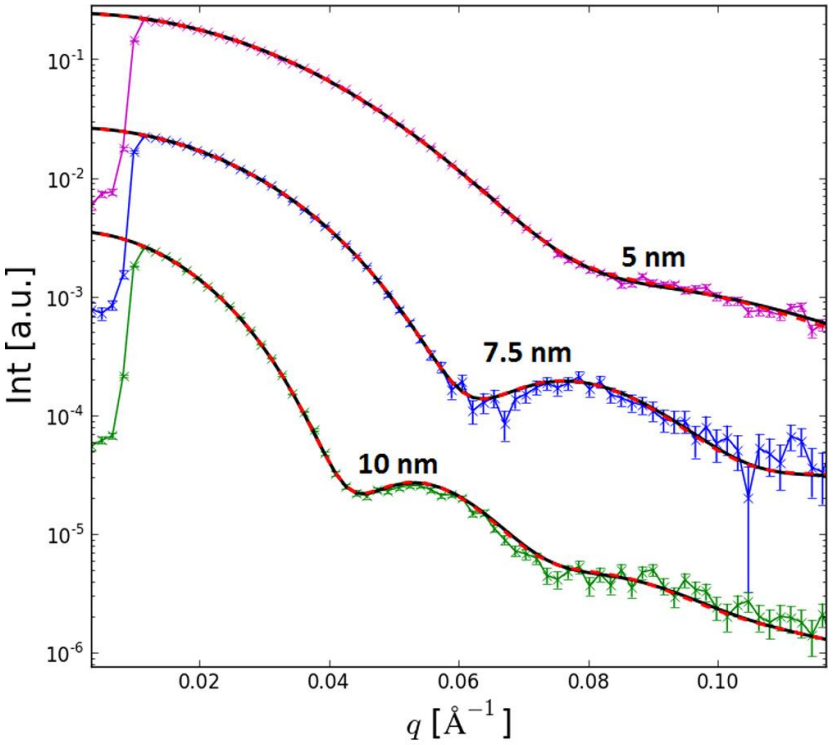
Size(S)

Shape | **Size**

SAXS	
Pros	**Cons**
Sample in suspension	More complex to analyze data than TEM

- Elemental size:
  - TEM, SEM
  - AFM
  - XRD
  - SAXS Small-angle X-ray scattering
    - Sample in suspension
    - Scattering of X-Ray gives information of NPs elemental size





https://doi.org/10.1016/j.nimb.2014.11.049

Size(S)

Shape | **Size**

- Elemental size:
  - TEM, SEM
  - AFM
  - XRD
  - SAXS
  - BET (details later)
    - Minimum 50-100 mg (see part SSA)
    - For non porous material
    - Spherical approximation

Equation linking surface area and size

$$\phi_{BET} = \frac{6000}{\rho \times S_{BET}}$$

ϕ_{BET} : Size of the sphere of S_{BET} surface area in nm
S_{BET} : Specific surface area of NPs in $m^2.g^{-1}$
ρ : density of the NPs in $g.cm^{-3}$

Why 6000?

$$Surface_{Sphere} = 4\pi\frac{\phi^2}{4} = \pi\phi^2$$

$$Volume_{Sphere} = \frac{4}{3}\pi\frac{\phi^3}{8} = \frac{\pi\phi^3}{6}$$

$$S_{BET} = \frac{S_{NP}}{m_{NP}} = \frac{S_{NP}}{d * V_{NP}} = \frac{\pi\phi^2}{d * \frac{\pi\phi^3}{6}} = \frac{6\phi^2}{d * \phi^3} \overset{units}{\Longrightarrow} \frac{6}{d * \phi}$$

Dimensional analysis of equation

$$S_{BET} = \frac{m^2}{g} = \frac{6(m^2)}{(g/cm^3) * (nm^3)} = \frac{6\,(m^2)}{g * \frac{(m^3) * 10^{-9}}{(m^3) * 10^{-6}}} = \frac{6000(m^2)}{(g)}$$

$$S_{BET} = \frac{6000}{\rho \times \phi_{BET}}$$

Size(S)

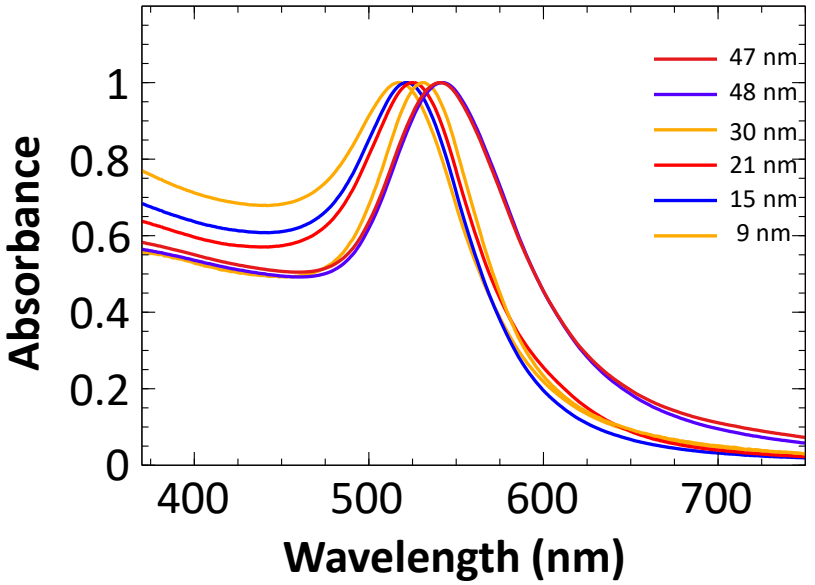
Shape | **Size**

UV-visible	
Pros	**Cons**
Easy to use	Only for plasmonic NPs
Not destructive	Calculation not accurate

- Elemental size:
  - TEM, SEM
  - AFM
  - XRD
  - SAXS
  - BET
  - UV-Visible
    - Suspension as such or diluted
    - For Gold NPs with Plasmon resonance

$$\phi_{Plasmon} = \exp(B_1 \frac{A_{SPR}}{A_{450}} - B_2)$$

$\phi_{Plasmon}$: Size of the gold NP
A_{SPR} : Absorbance at the surface Plasmon resonance
A_{450} : Absorbance at 450 nm
B_1 = 3.00 and B_2 = 2.20 experimentally determined

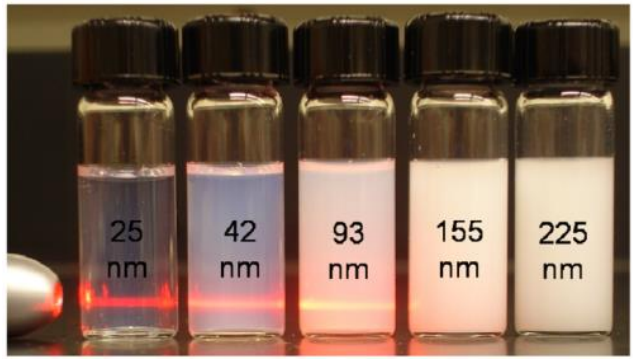


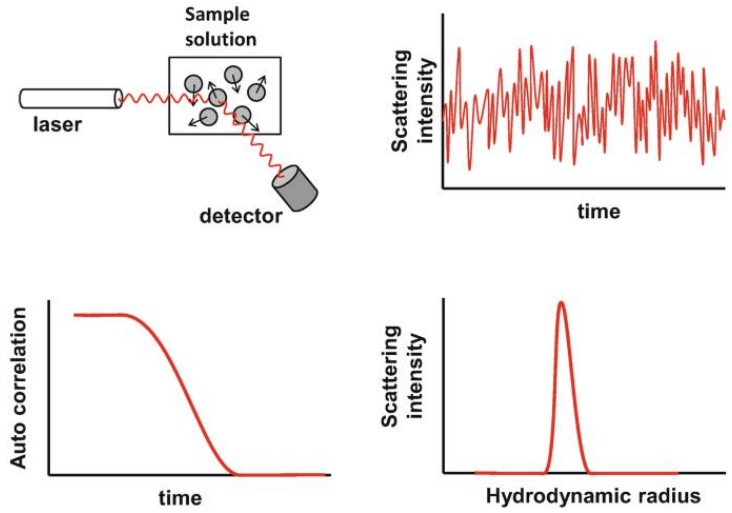
https://doi.org/10.1021/ac0702084

Size(S)

Shape | Size | **Aggregation**

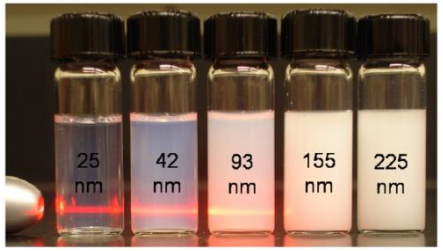
- Size in suspension:
  - DLS Dynamic Light Scattering
    - For NPs in suspension
    - Light scattered by NPs

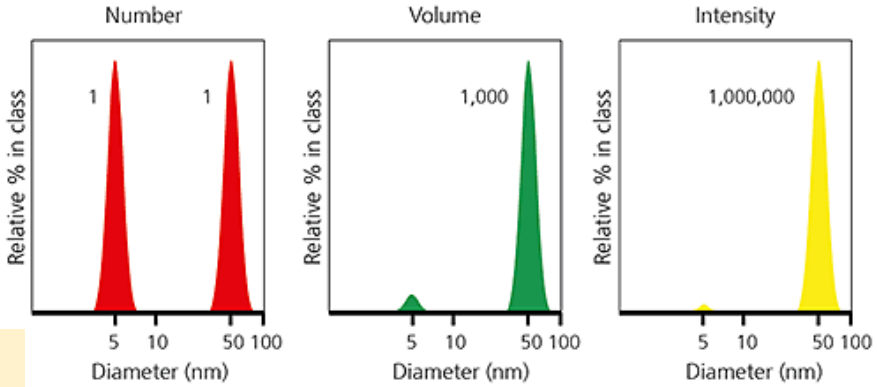




Size(S)

Shape → Size → **Aggregation**

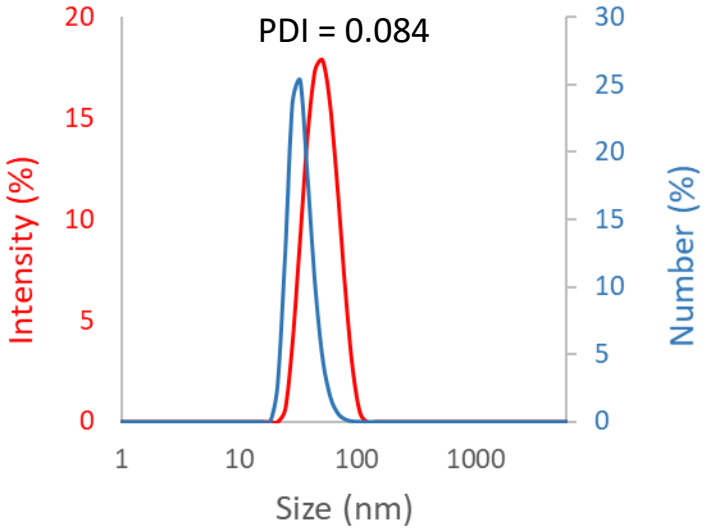




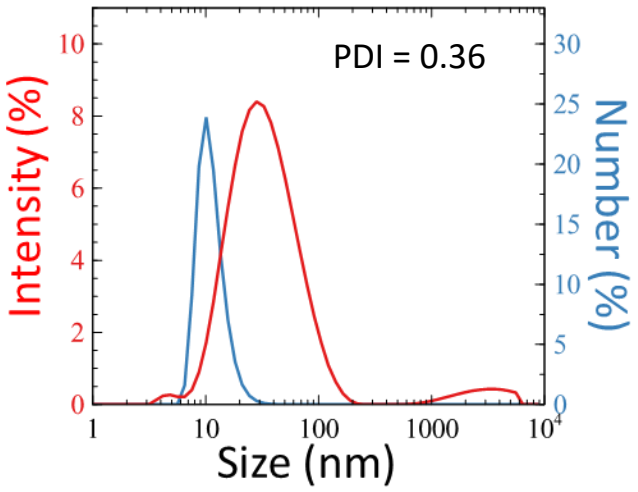
- Size in suspension:
  - DLS Dynamic Light Scattering
    - For NPs in suspension
    - Light scattered by NPs
    - Sensitive to big NPs (~d^6 intensity)
      - Polydispersity index (PDI)
    - Spherical assumption

PDI [0 - 1]
PDI < 0.1 : monodisperse NPs
PDI > 0.1 Polydisperse NPs

Example of monodisperse NPs



Example of polydisperse NPs



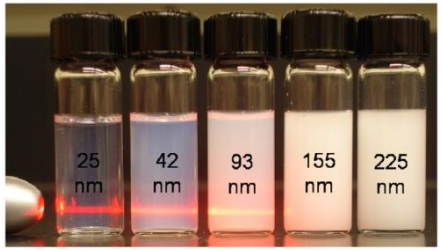
Equation Stokes-Einstein-Sutherland

$$D = \frac{k_B T}{6\pi\eta r}$$

D : diffusion of spherical particle
T : temperature
k_B : Boltzmann constant
η : dynamic viscosity
r : radius of a spherical particle

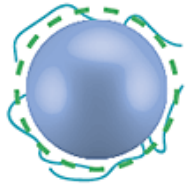
Size(S)

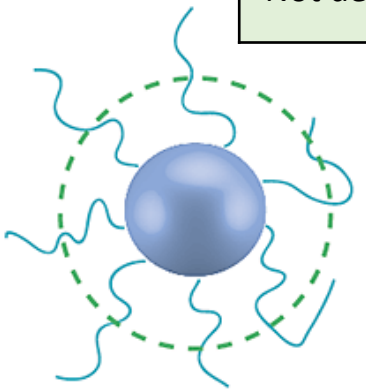
Shape → Size → **Aggregation**

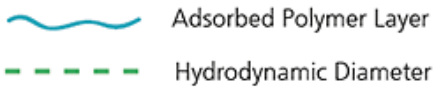


DLS	
Pros	**Cons**
Easy to use	Sphere only?
Few volume	Sensitive to big NPs and high PDI
Not destructive?	Solution conditions

- Size in suspension:
  - DLS Dynamic Light Scattering
    - For NPs in suspension
    - Light scattered by NPs
    - Sensitive to big NPs (~d^6 intensity)
      - Polydispersity index (PDI)
    - Spherical assumption
    - Hydrodynamic layer
      - Be careful ionic strength and pH







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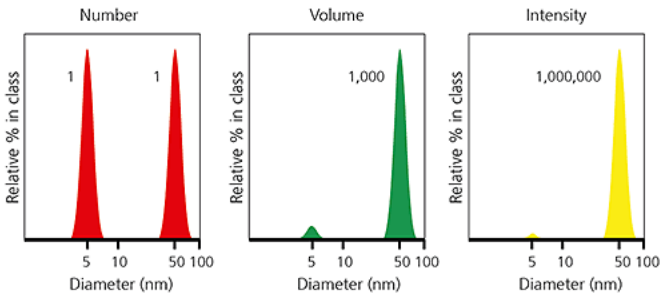
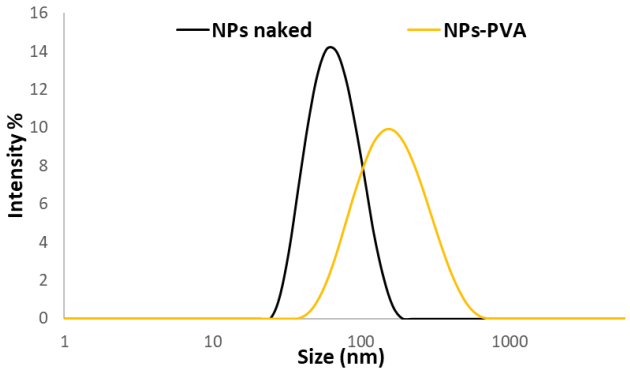




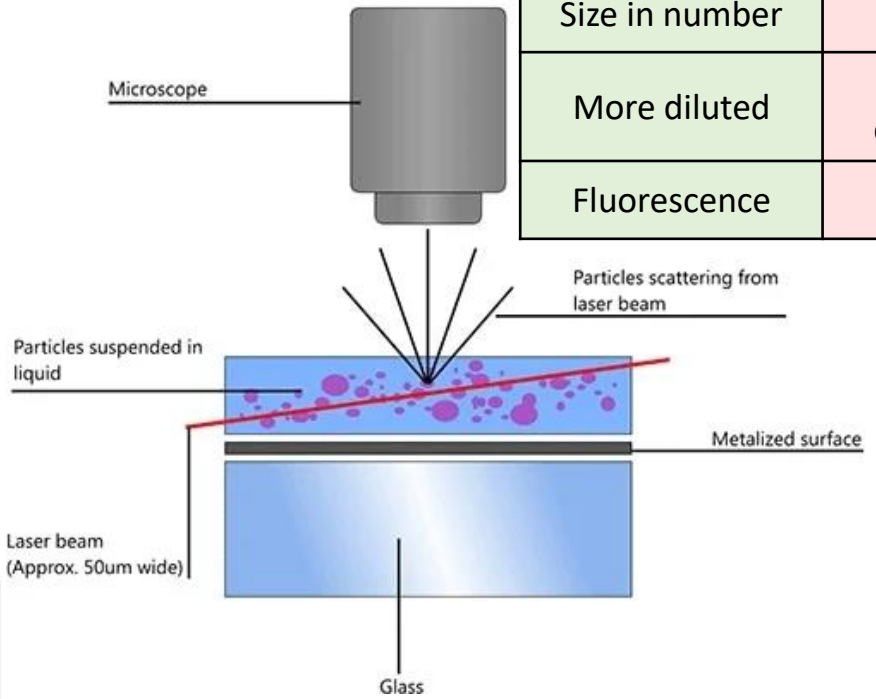
Influence of coatings on NPs

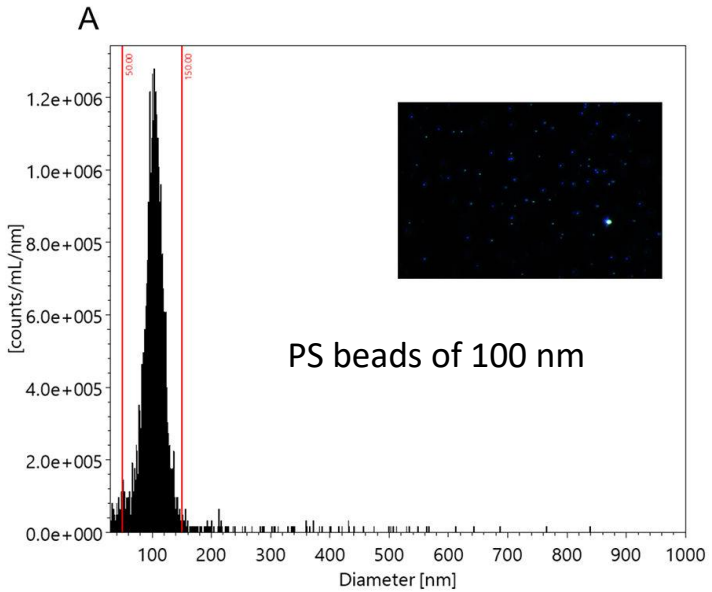
Size(S)

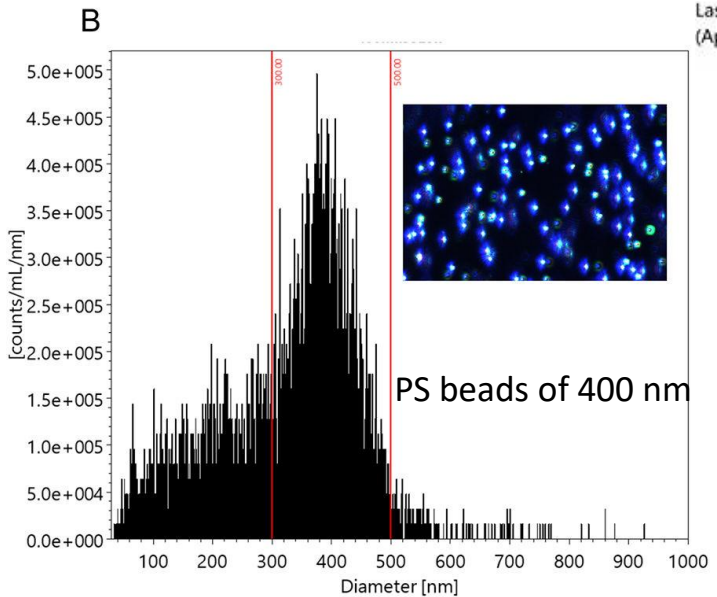
Shape → Size → **Aggregation**

NTA vs DLS	
Pros	**Cons**
Visual results	[10 – 1000] nm
Size in number	Slower
More diluted	Less concentrated
Fluorescence	

- Size in suspension:
  - DLS
  - NTA Nanoparticle Tracking Analysis
    - For NPs in suspension
    - NPs illuminated by laser and scattered light collected in a microscope captured and analyzed by camera
    - Similar to DLS for calculation







https://doi.org/10.3791%2F62447

Size(S)

Shape | Size | **Aggregation**

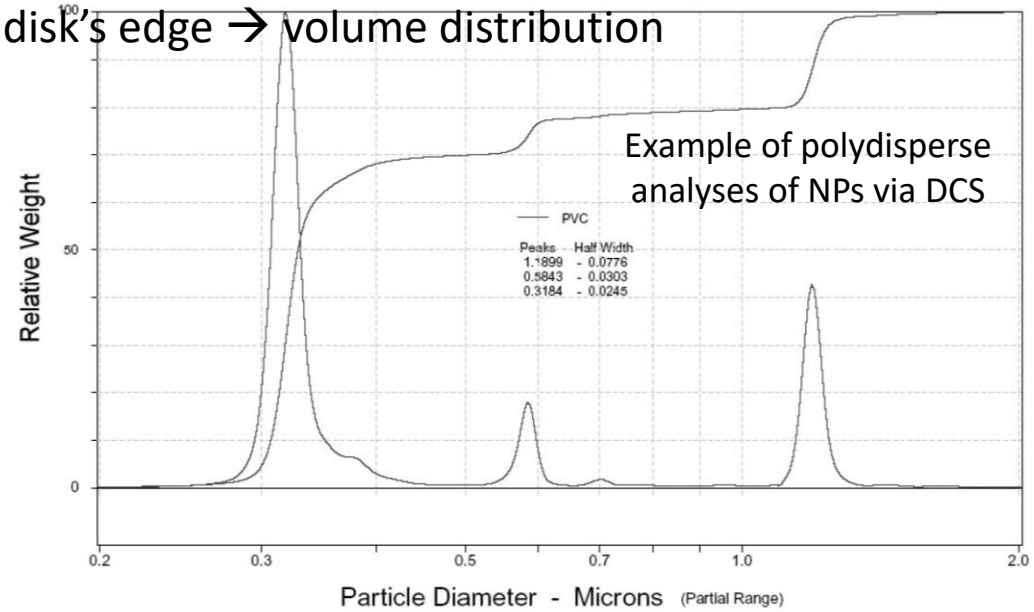
DCS vs DLS	
Pros	**Cons**
Volume not Intensity	Gradient to prepare
More precise	Destructive
Density if size known	

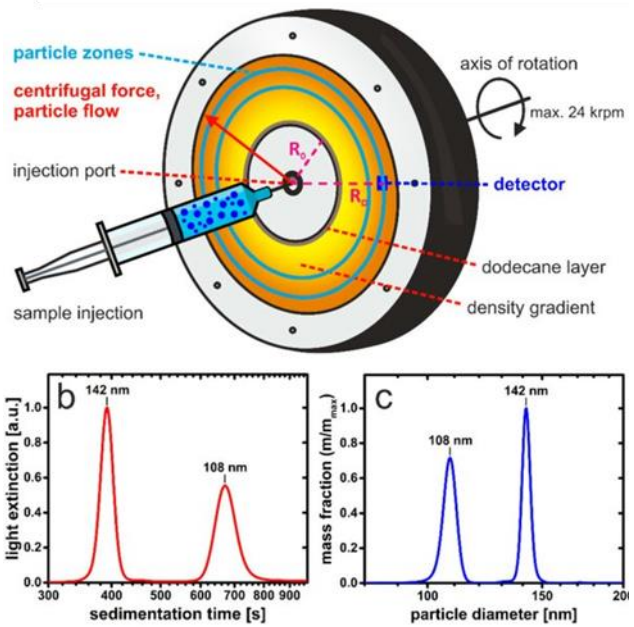
- Size in suspension:
  - DLS
  - NTA
  - DCS differential centrifugal sedimentation

    NP Suspension in spinning disk

    NPs migrate from center to edge of disk in a sucrose gradient solution

    NPs measure at disk's edge → volume distribution





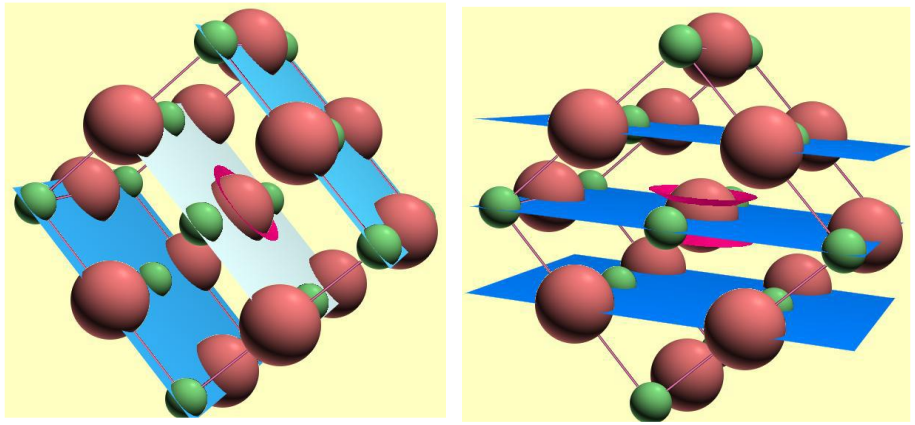
Crystallinity & Chemistry

Shape → Size → Aggregation → **Crystallinity**

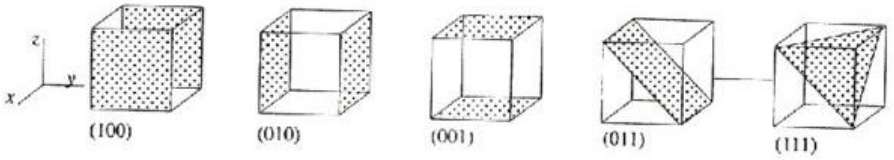
- Crystallinity of NPs is an important parameter to analyze
- It is usually link to chemical characterization
  - X-Rays apparatus are the most used methods

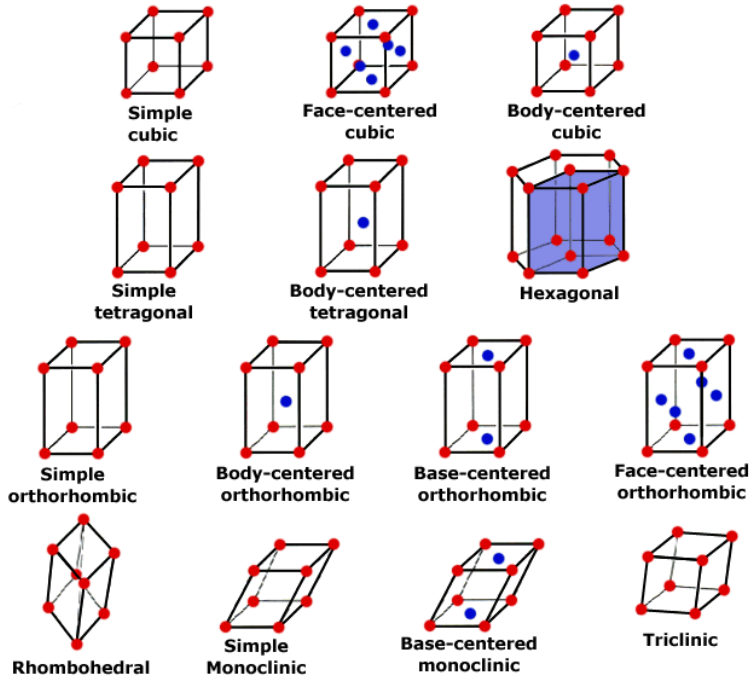
Crystal System Table

System	Axial length	Axial Angle	Unit Cell Geometry
Cubic	a = b = c	α = β = γ = 90°	
Tetragonal	a = b ≠ c	α = β = γ = 90°	
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°	
Rhombohedral	a = b = c	α = β = γ ≠ 90°	
Hexagonal	a = b ≠ c	α = β = 90°, γ=120°	
Monoclinic	a ≠ b ≠ c	α = γ = 90°, β≠90°	
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ	



Each crystal is organized with different lattice plan
These plans diffract X-Rays



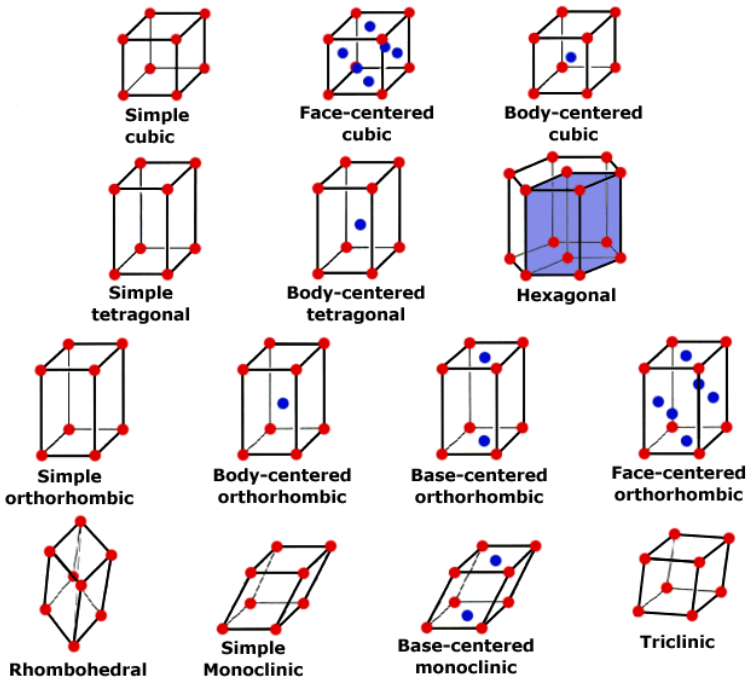


Crystallinity & Chemistry

Shape → Size → Aggregation → **Crystallinity**

Triclinique		
1	P 1	1
2	P -1	$\bar{1}$
Monoclinique		
3	P 2	2
4	$P 2_1$	
5	C 2	
6	P m	m
7	P c	
8	C m	
9	C c	
10	P 2/m	2/m
11	$P 2_1/m$	
12	C 2/m	
13	P 2/c	
14	$P 2_1/c$	
15	C 2/c	
Orthorhombique		
16	P 2 2 2	2 2 2
17	P 2 2 2_1	
18	$P 2_1 2_1 2$	
19	$P 2_1 2_1 2_1$	
20	C 2 2 2_1	
21	C 2 2 2	
22	F 2 2 2	
23	I 2 2 2	
24	$I 2_1 2_1 2_1$	
25	P m m 2	m m 2
26	P m $c 2_1$	
27	P c c 2	
28	P m a 2	
29	P c $a 2_1$	
30	P n c 2	
31	P m $n 2_1$	
32	P b a 2	
33	P n $a 2_1$	
34	P n n 2	
35	C m m 2	
36	C m $c 2_1$	
37	C c c 2	
38	A m m 2	
39	A b m 2	
40	A m a 2	
41	A b a 2	
42	F m m 2	
43	F d d 2	
44	I m m 2	
45	I b a 2	
46	I m a 2	
47	P m m m	m m m
48	P n n n	
49	P c c m	
50	P b a n	
51	P m m a	
52	P n n a	
53	P m n a	
54	P c c a	
55	P b a m	
56	P c c n	
57	P b c m	
58	P n n m	
59	P m m n	
60	P b c n	
61	P b c a	
62	P n m a	
63	C m c m	
64	C m c a	
65	C m m m	
66	C c c m	
67	C m m a	
68	C c c a	
69	F m m m	
70	F d d d	
71	I m m m	
72	I b a m	
73	I b c a	
74	I m m a	
Tétragonal		
75	P 4	4
76	P 4_1	
77	P 4_2	
78	P 4_3	
79	I 4	
80	$I 4_1$	
81	P -4	$\bar{4}$
82	I -4	
83	P 4/m	4/m
84	$P 4_2/m$	
85	P 4/n	
86	$P 4_2/n$	
87	I 4/m	
88	$I 4_1/a$	
89	P 4 2 2	4 2 2
90	P 4 2_1 2	
91	P 4_1 2 2	
92	P 4_1 2_1 2	
93	P 4_2 2 2	
94	P 4_2 2_1 2	
95	P 4_3 2 2	
96	P 4_3 2_1 2	
97	I 4 2 2	
98	$I 4_1$ 2 2	
99	P 4 m m	4 m m
100	P 4 b m	
101	P 4_2 c m	
102	P 4_2 n m	
103	P 4 c c	
104	P 4 n c	
105	P 4_2 m c	
106	P 4_2 b c	
107	I 4 m m	
108	I 4 c m	
109	$I 4_1$ m d	
110	$I 4_1$ c d	
111	P -4 2 m	$\bar{4}$ 2 m
112	P -4 2 c	
113	P -4 2_1 m	
114	P -4 2_1 c	
115	P -4 m 2	4/m m m
116	P -4 c 2	
117	P -4 b 2	
118	P -4 n 2	
119	I -4 m 2	
120	I -4 c 2	
121	I -4 2 m	
122	I -4 2 d	
123	P 4/m m m	
124	P 4/m c c	
125	P 4/n b m	
126	P 4/n n c	
127	P 4/m b m	
128	P 4/m n c	
129	P 4/n m m	
130	P 4/n c c	
131	$P 4_2/m m c$	
132	$P 4_2/m c m$	
133	$P 4_2/n b c$	
134	$P 4_2/n n m$	
135	$P 4_2/m n m$	
136	$P 4_2/m b c$	
137	$P 4_2/n m c$	
138	$P 4_2/n c m$	
139	I 4/m m m	
140	I 4/m c m	
141	$I 4_1/a m d$	
142	$I 4_1/a c d$	
Rhomboédrique		
143	P 3	3
144	$P 3_1$	
145	$P 3_2$	
146	R 3	
147	P -3	$\bar{3}$
148	R -3	
149	P 3 1 2	3 2
150	P 3 2 1	
151	$P 3_1$ 1 2	
152	$P 3_1$ 2 1	
153	$P 3_2$ 1 2	
154	$P 3_2$ 2 1	
155	R 3 2	
156	P 3 m 1	3 m
157	P 3 1 m	
158	P 3 c 1	
159	P 3 1 c	
160	R 3 m	
161	R 3 c	
162	P -3 1 m	$\bar{3}$ m
163	P -3 1 c	
164	P -3 m 1	
165	P -3 c 1	
166	R -3 m	
167	R -3 c	
Hexagonal		
168	P 6	6
169	$P 6_1$	
170	$P 6_5$	
171	$P 6_2$	
172	$P 6_4$	
173	$P 6_3$	
174	P -6	$\bar{6}$
175	P 6/m	6/m
176	$P 6_3/m$	
177	P 6 2 2	6 2 2
178	P 6_1 2 2	
179	P 6_5 2 2	
180	P 6_2 2 2	
181	P 6_4 2 2	
182	P 6_3 2 2	
183	P 6 m m	6 m m
184	P 6 c c	
185	P 6_3 c m	
186	P 6_3 m c	
187	P -6 m 2	$\bar{6}$ m 2
188	P -6 c 2	
189	P -6 2 m	
190	P -6 2 c	
191	P 6/m m m	6/m m m
192	P 6/m c c	
193	$P 6_3/m c m$	
194	$P 6_3/m m c$	
Cubique		
195	P 2 3	2 3
196	F 2 3	
197	I 2 3	
198	$P 2_1$ 3	
199	$I 2_1$ 3	
200	P m 3	m 3
201	P n 3	
202	F m 3	
203	F d 3	
204	I m 3	
205	P a 3	
206	I a 3	
207	P 4 3 2	4 3 2
208	$P 4_2$ 3 2	
209	F 4 3 2	
210	F 4_1 3 2	
211	I 4 3 2	
212	P 4_3 3 2	
213	P 4_1 3 2	
214	$I 4_1$ 3 2	
215	P -4 3 m	$\bar{4}$ 3 m
216	F -4 3 m	
217	I -4 3 m	
218	P -4 3 n	
219	F -4 3 c	
220	I -4 3 d	
221	P m 3 m	m 3 m
222	P n 3 n	
223	P m 3 n	
224	P n 3 m	
225	F m 3 m	
226	F m 3 c	
227	F d 3 m	
228	F d 3 c	
229	I m 3 m	
230	I a 3 d	

All crystal systems are organized in space groups

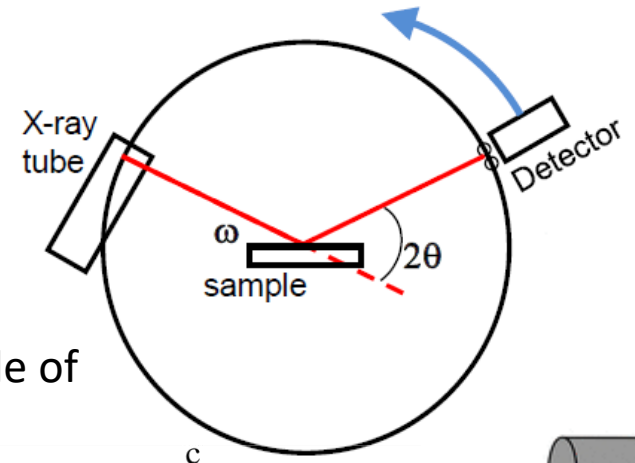


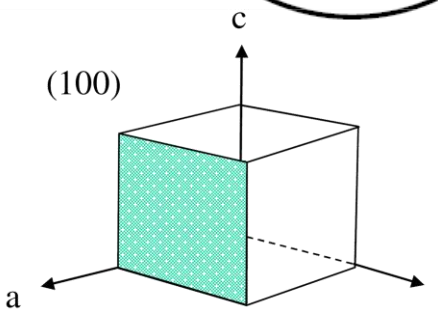
Crystallinity & Chemistry

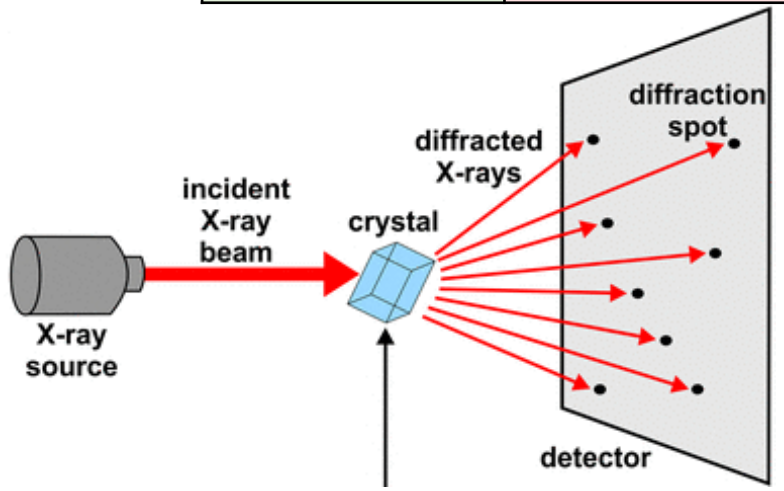
Shape | Size | Aggregation | **Crystallinity**

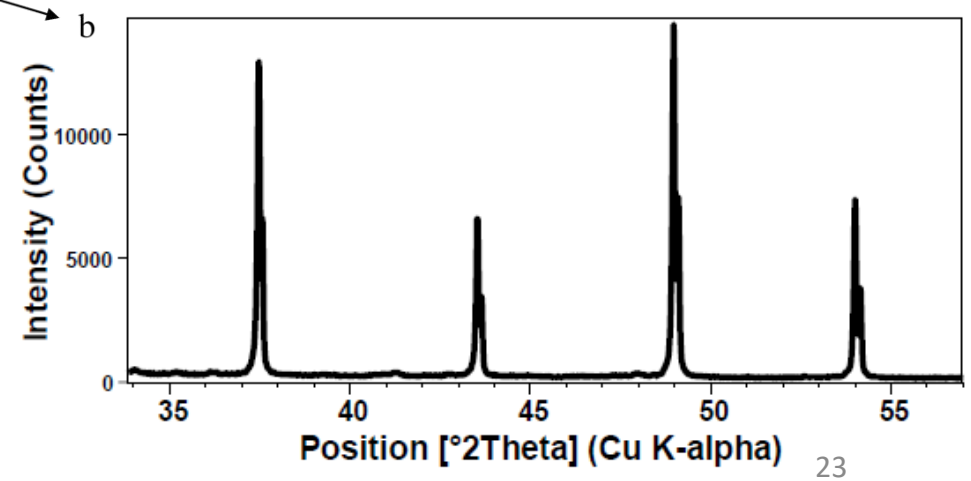
XRD	
Pros	**Cons**
Size, chemistry, crystallinity	For crystals
	Need a lot of powder

- XRD X-Ray Diffraction
  - X-Ray will diffract following their plan
    - Plan is directly linked to diffraction angle of orientation of the nanopowder: 2θ









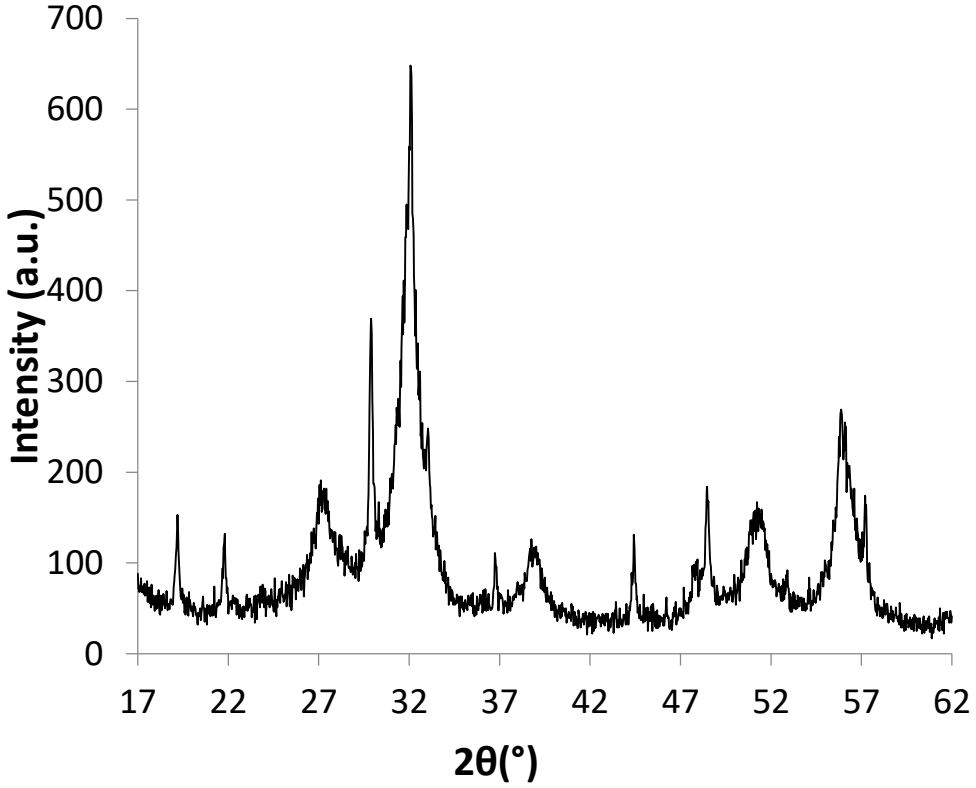
$$\lambda = 2d_{hkl}sin\theta$$

Bragg's Law
λ : Wavelength of XRD
d_{hkl} : interreticular distance
θ : Angle of diffraction in rad

Crystallinity & Chemistry

Shape | Size | Aggregation | **Crystallinity**

- XRD X-Ray Diffraction
  - X-Ray will diffract following their plan
  - Phase identification



Crystallinity & Chemistry

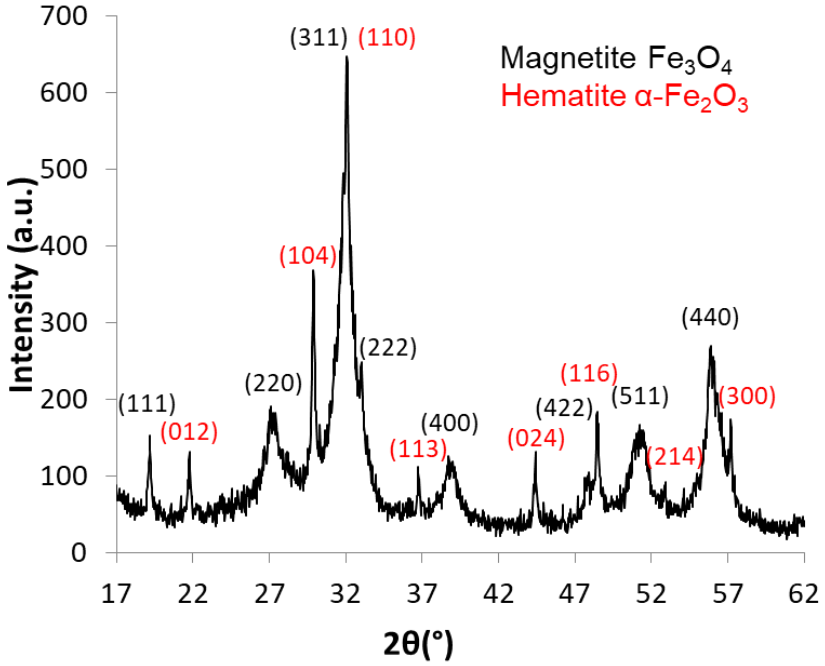
Shape | Size | Aggregation | **Crystallinity**

- XRD X-Ray Diffraction
  - X-Ray will diffract following their plan
  - Phase identification
    - With ICDD files International Centre for Diffraction Data
    - Quantification of phases possible

  In this example 12% of hematite.

$$\frac{I_{104}}{I_{220}} = 15.471 * x_{\alpha Fe2O3}$$

I_{hkl} : Intensity of peak of lattice planes
x_{Fe2O3} : mass proportion of α-Fe_2O_3



2θ(°)	Intensity	h	k	l
18.56	100	1	1	1
21.78	297	0	1	2
27.20	296	2	2	0
29.86	999	1	0	4
32.01	999	3	1	1
32.10	689	1	1	0
33.47	77	2	2	2
35.32	22	0	0	6
36.76	191	1	1	3
38.84	202	4	0	0
39.13	25	2	0	2
42.49	6	3	3	1
44.41	298	0	2	4
48.06	83	4	2	2
48.46	403	1	1	6
50.34	2	2	1	1
51.18	271	5	1	1
51.54	64	1	2	2
51.54	64	0	1	8
55.84	225	2	1	4
56.10	354	4	4	0
57.22	235	3	0	0

Crystallinity & Chemistry

Shape | Size | Aggregation | **Crystallinity**

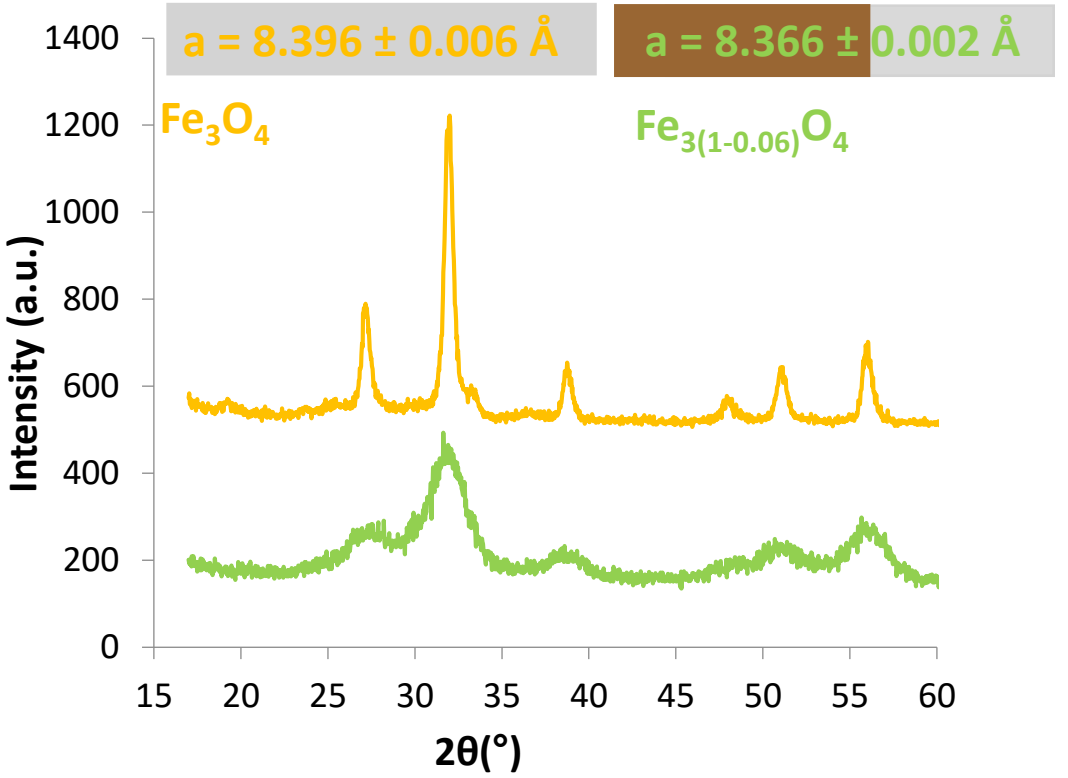
- XRD X-Ray Diffraction
  - X-Ray will diffract following their plan
  - Phase identification
  - Lattice parameter: precise chemistry of oxidation
    - For cubic space groups lattice parameter **a**:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

    - With accurate fitting of diffraction patterns distinction of oxidation state

System	Axial length	Axial Angle	Unit Cell Geometry
Cubic	a = b = c	α = β = γ = 90°	

Maghemite γ-Fe_2O_3	$Fe_{3(1-\delta)}O_4$	Magnetite Fe_3O_4
a = 8.345 Å	a = ? Å	a = 8.396 Å



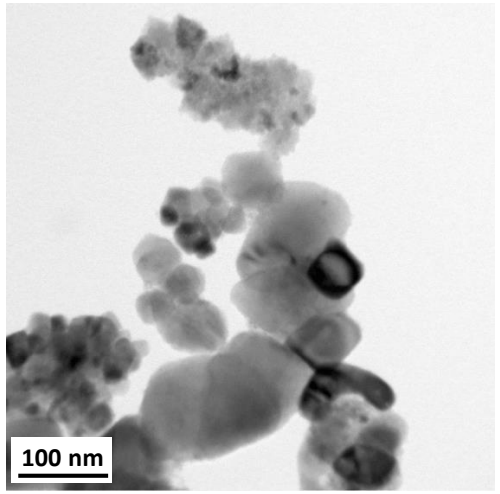
Crystallinity & Chemistry

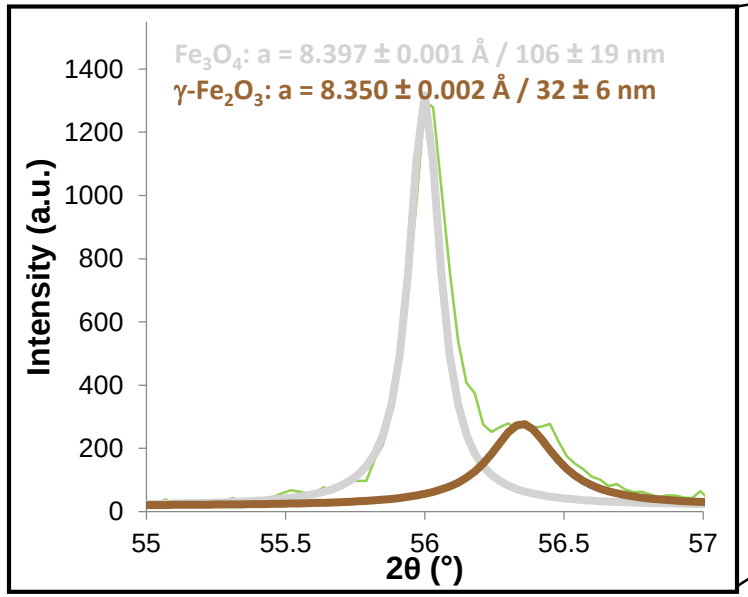
Shape → Size → Aggregation → **Crystallinity**

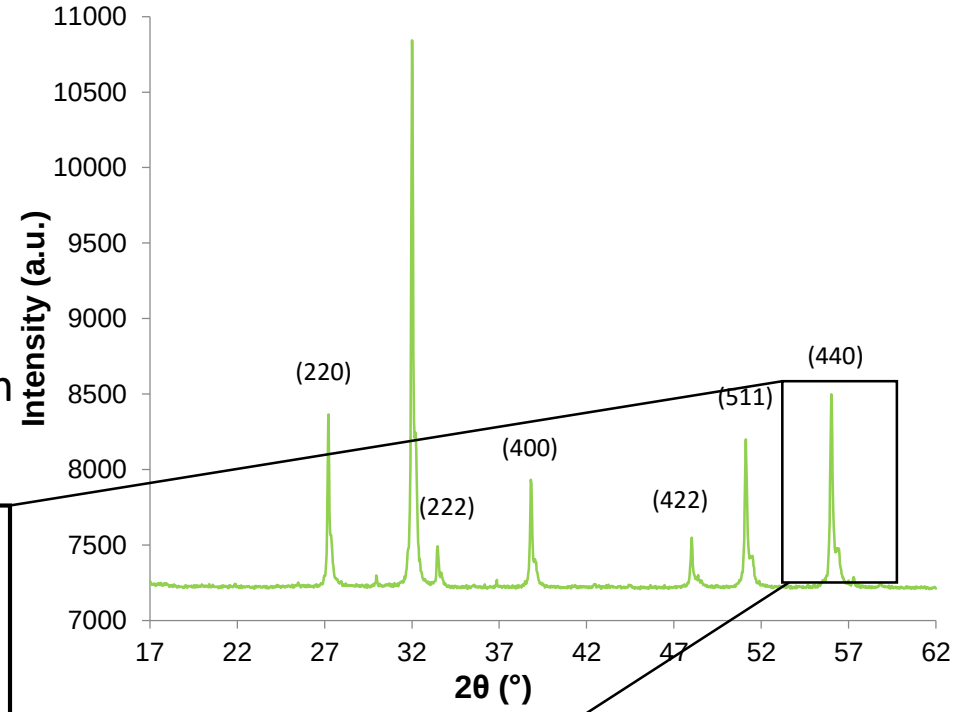
Maghemite γ-Fe_2O_3	Magnetite Fe_3O_4
a = 8.345 Å	a = 8.396 Å

- XRD X-Ray Diffraction
  - X-Ray will diffract following their plan
  - Phase identification
  - Lattice parameter: precise chemistry of oxidation
    - With accurate fitting of diffraction patterns distinction of oxidation state

Iron oxides NPs





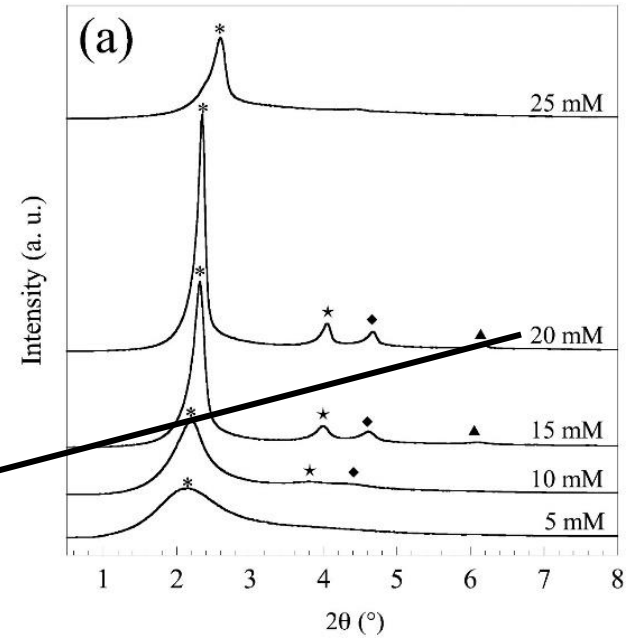


Crystallinity & Chemistry

Shape → Size → Aggregation → **Crystallinity**

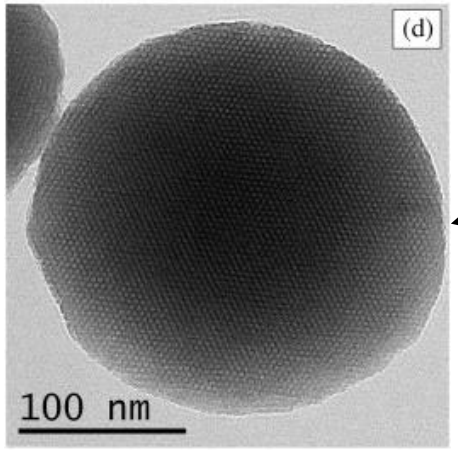
XRD	
Pros	**Cons**
Size, chemistry, crystallinity	For crystals
Periodicity of porous NPs	Need a lot of powder

- XRD X-Ray Diffraction
  - X-Ray will diffract following their plan
  - Phase identification
  - Lattice parameter: precise chemistry of oxidation
  - Periodicity
    - In the case of ordered mesoporous structures, XRD at small angles can give information of pore size and organization



XRD patterns of a) calcined Mesoporous Silica NPs synthesized with 5, 10, 15, 20 and 25 mM of NaOH

Lattice parameter *e.g.* distance between pores: 4.38 nm

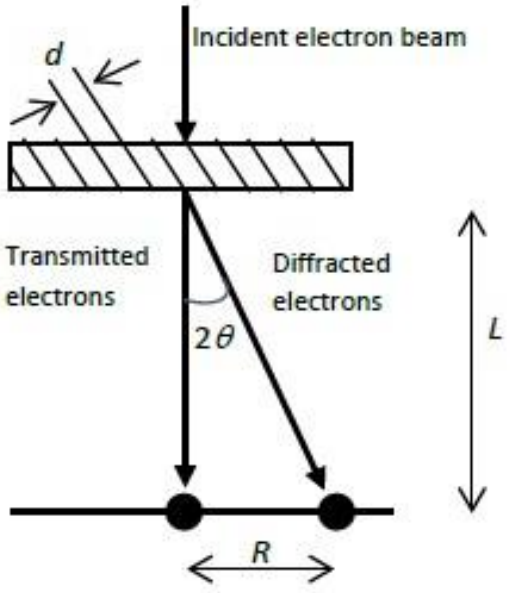


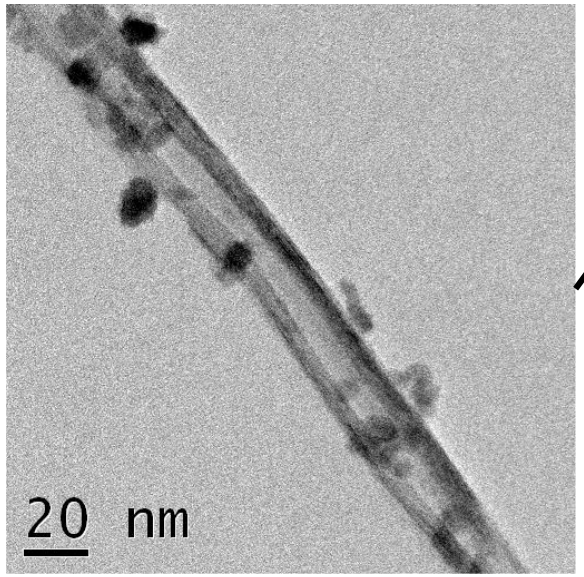
https://doi.org/10.1016/j.jnoncrysol.2014.10.020

Crystallinity & Chemistry

Shape | Size | Aggregation | **Crystallinity**

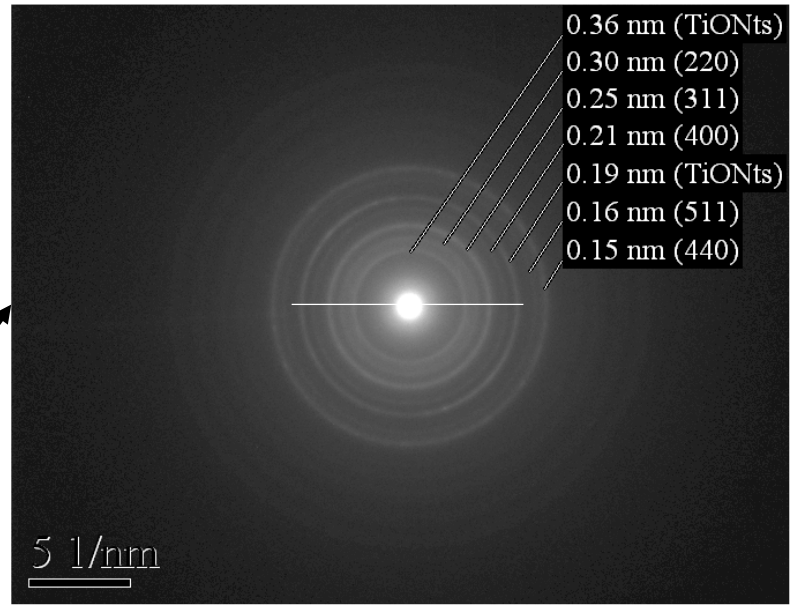
- XRD X-Ray Diffraction
- TEM (or SEM)
  - SAD Selected area diffraction
    - Electronic diffraction





https://doi.org/10.1021/jp2056893

Electronic diffraction of Titanate NTs and Fe_3O_4 NPs



$$\lambda = 2d_{hkl}sin\theta$$

ICDD

d_{hkl} (nm)	Intensity	h	k	l
0.30	296	2	2	0
0.25	999	3	1	1
0.21	202	4	0	0
0.16	271	5	1	1
0.15	354	4	4	0

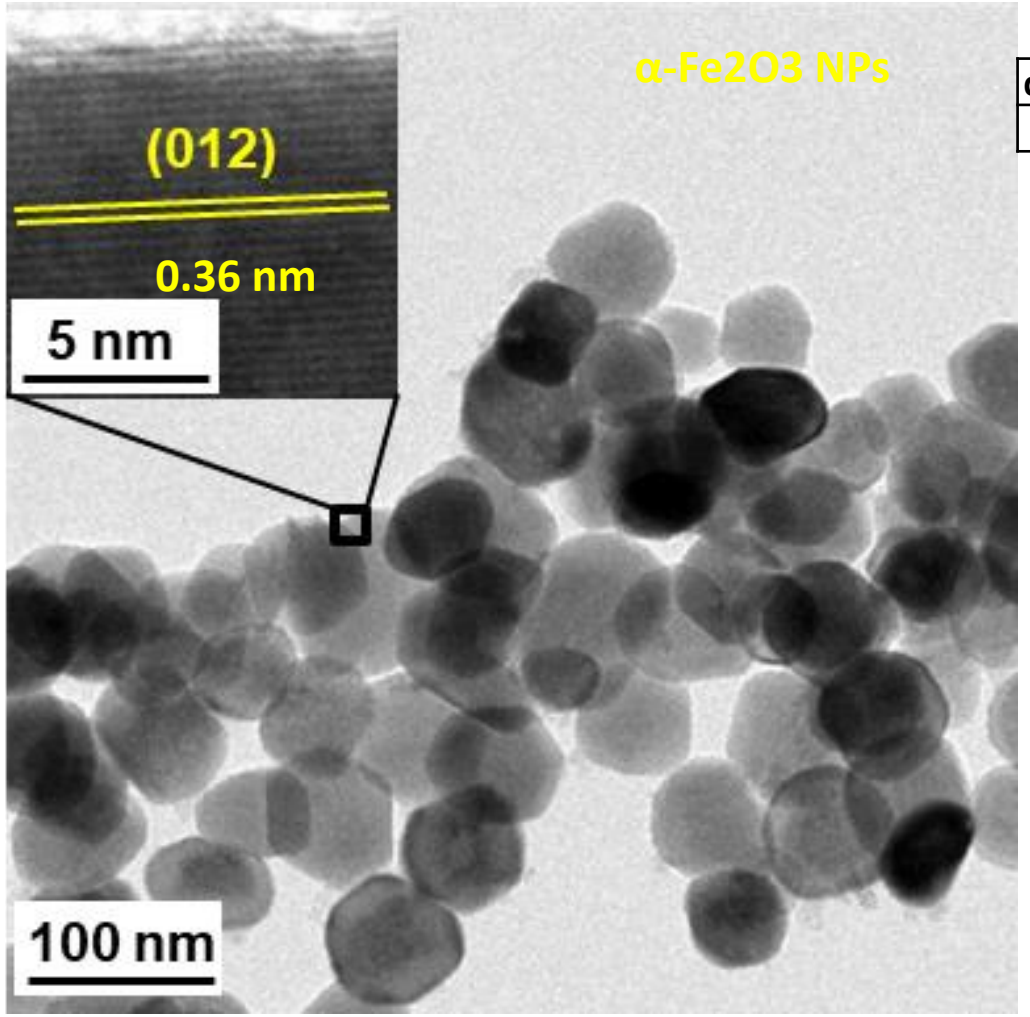
Magnetite Fe_3O_4

Crystallinity & Chemistry

Shape → Size → Aggregation → **Crystallinity**

TEM vs XRD	
Pros	**Cons**
1 NP analyzable Lower quantity	Less representative

- XRD X-Ray Diffraction
- TEM (or SEM)
  - SAD Selected area diffraction
  - High Resolution TEM



ICDD

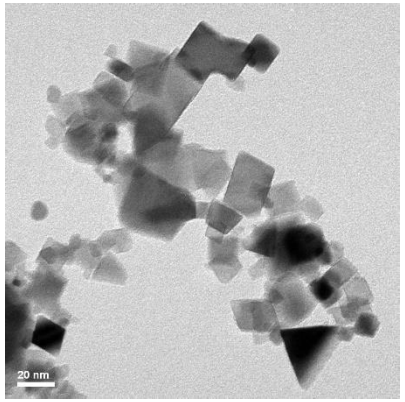
d (nm)	Intensity	h	k	l
0.36	297	0	1	2

https://doi.org/10.1039/C4RA08562K

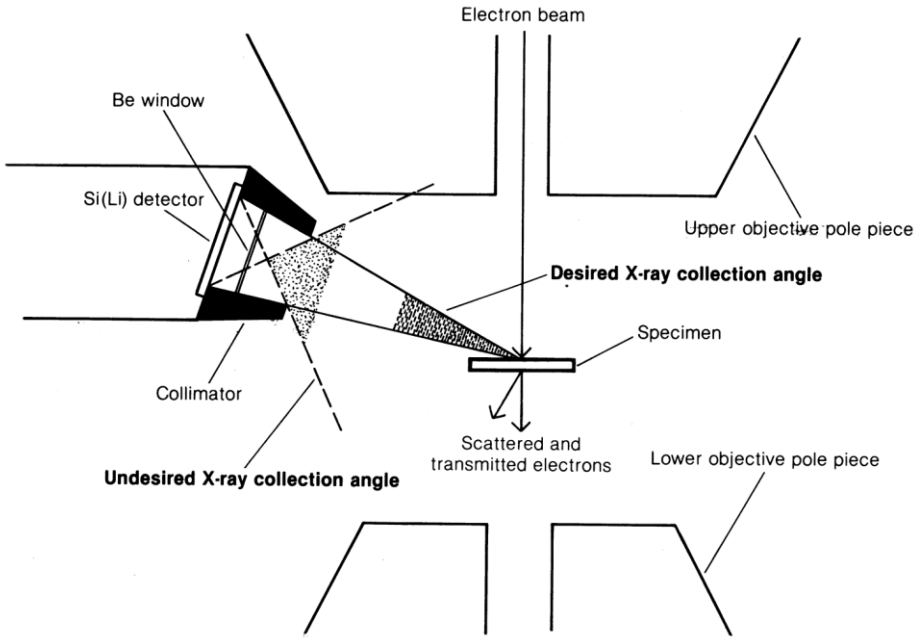
Crystallinity & Chemistry

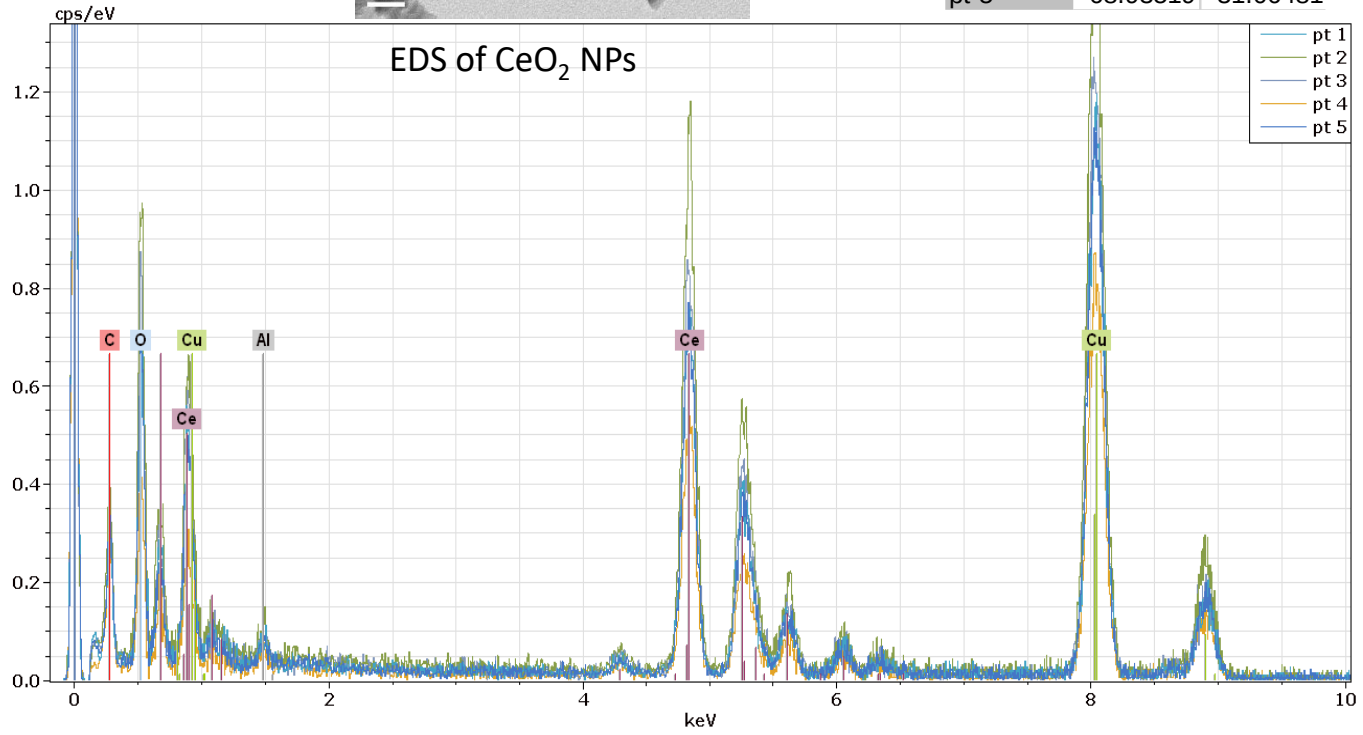
Shape | Size | Aggregation | Crystallinity | **Chemistry**

- XRD X-Ray Diffraction
- TEM (or SEM)
  - EDS: Energy Dispersive X-ray Spectroscopy
    - Quantification
    - Scan of core/shell possible



Spectrum	O	Ce
pt 1	67.73074	32.26926
pt 2	68.45332	31.54668
pt 3	66.26656	33.73344
pt 4	64.88982	35.11018
pt 5	68.93519	31.06481



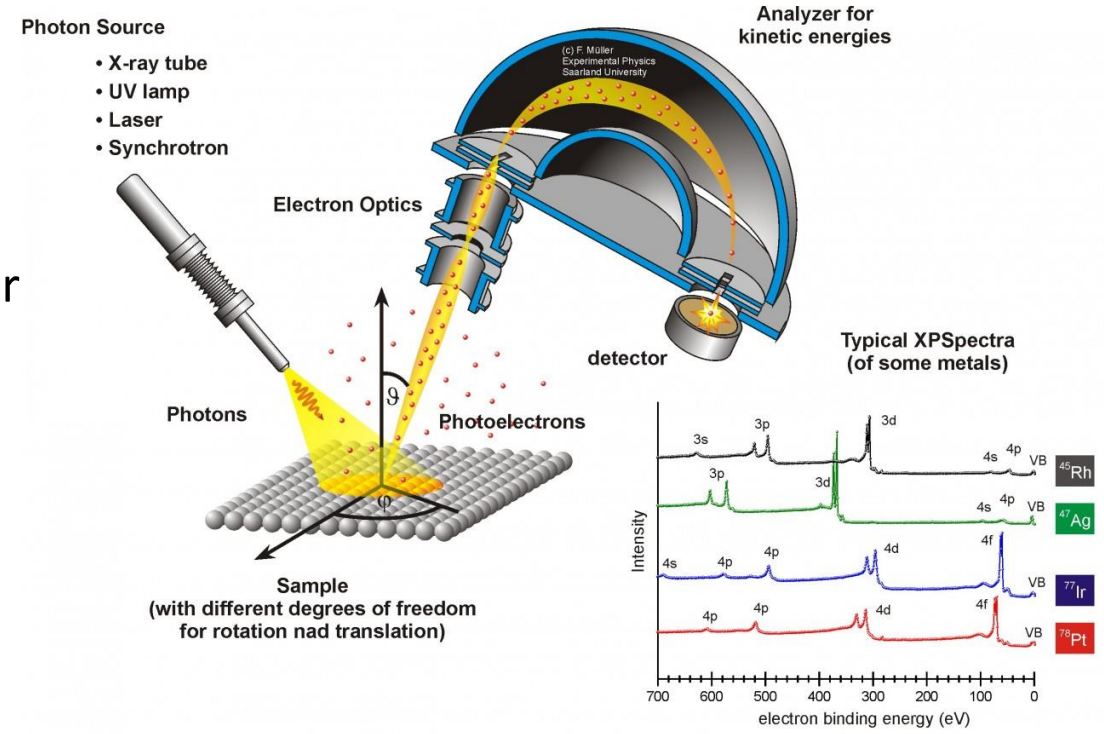


Crystallinity & Chemistry

Shape → Size → Aggregation → Crystallinity → **Chemistry**

XPS	
Pros	**Cons**
Effective for various chemistry	Powder
Can analyze contaminant	Only 10 nm depth

- XRD X-Ray Diffraction
- TEM (or SEM)
- XPS: X-Ray photoelectron spectroscopy
  - > 10 mg of powder
  - Surface analysis (~10 nm depth) so not suitable for some NPs
  - Important technique for surface chemistry

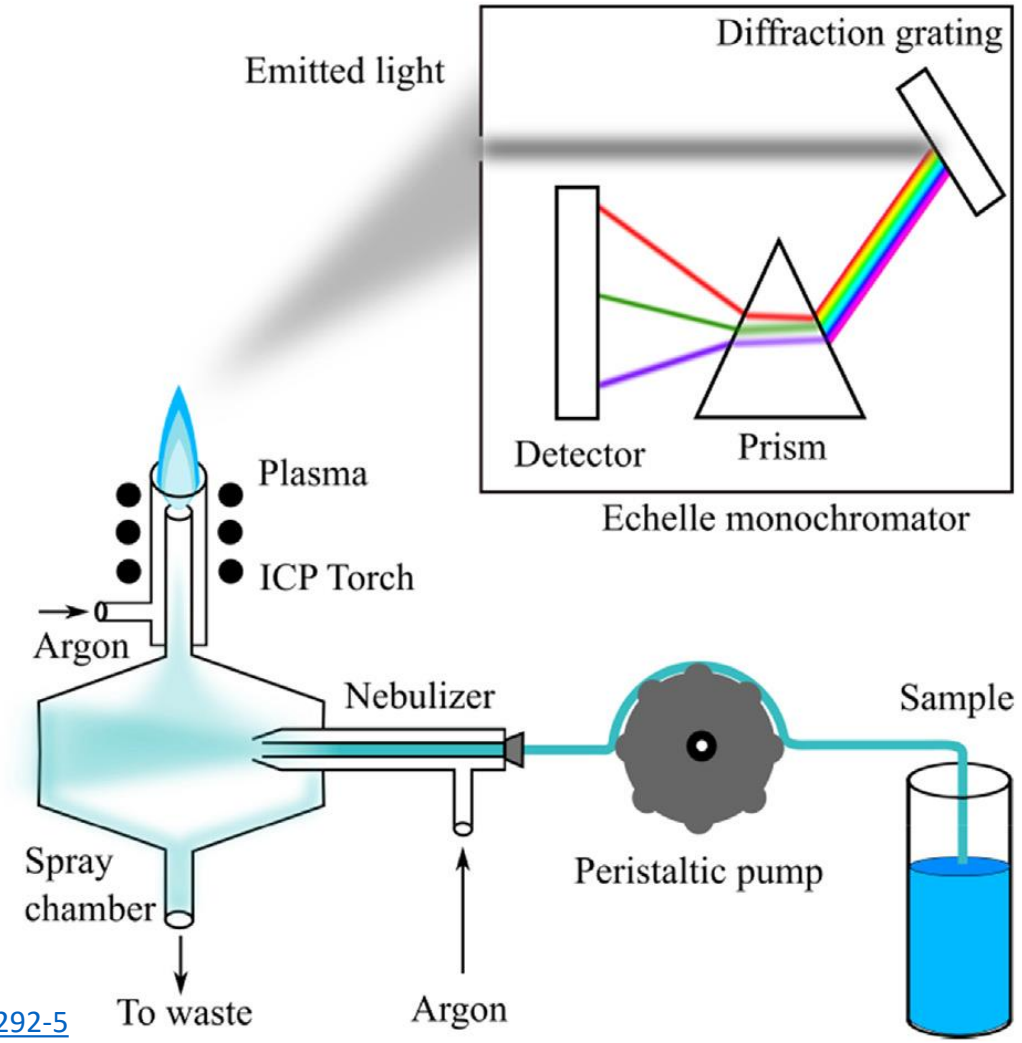


Crystallinity & Chemistry

Shape → Size → Aggregation → Crystallinity → **Chemistry**

ICP	
Pros	**Cons**
For all type NPs	Destructive
Sensitive	Not for organic

- XRD X-Ray Diffraction
- TEM (or SEM)
- XPS
- ICP Induced Coupled Plasma
  - Need to dissolve NP's suspension
  - Sensitivity 1 ppm to 1 ppb
  - Not suitable for C, N and O elements
- Chemical titrations

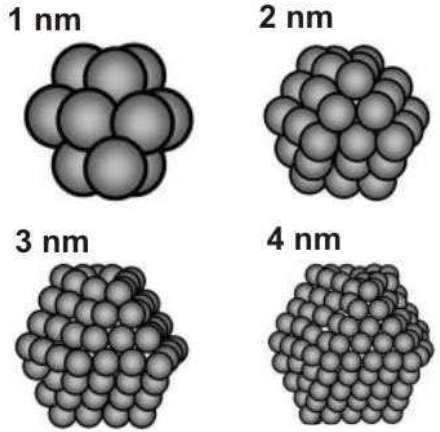


https://doi.org/10.1016/B978-0-12-409547-2.13292-5

Surface characterization

Shape | Size | Aggregation | Crystallinity | Chemistry

- Surface characterization
  - NPs have very high surface / volume ratio: > 50 m^2/g NPs
  - Surface is important for reactivity of NPs
    - For biology, this is the interface between your materials and the living system



- Parameters to study following ISO
  - Specific surface area
  - Surface charge
  - Surface chemistry

Particle diameter (nm)	Total number atoms	Total number surface atoms	Surface atoms / Total atoms (%)
1	76	76	100
2	610	303	50.2
5	9541	1897	19.7
10	76332	7591	9.9
20	610658	30364	4.9
50	9541533	189779	1.9
100	76103500	757600	1.0

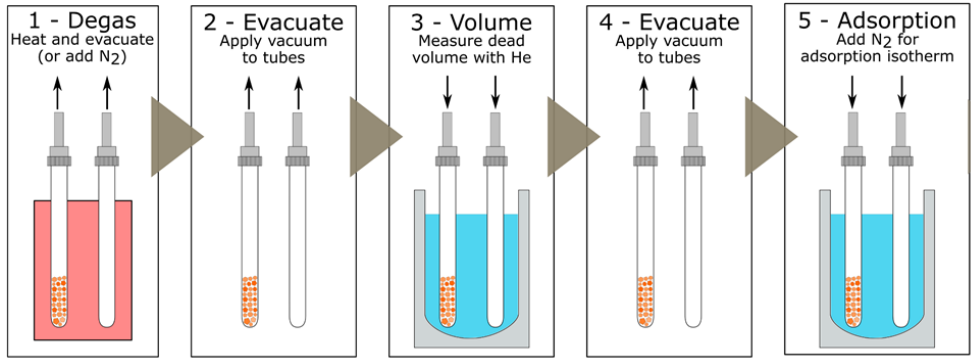
https://doi.org/10.5772/35238

Surface characterization

Shape | Size | Aggregation | Crystallinity | Chemistry | **SSA**

BET	
Pros	**Cons**
Easy to use	Long
Pore and sizes	Need 10 mg of powder

- BET Brunauer, Emmett and Teller
  - Dried powder: isothermal adsorption of gas
    - Powder for ~10 m² (50/100 mg)
    - SSA in m²/g
    - Pores characterizations

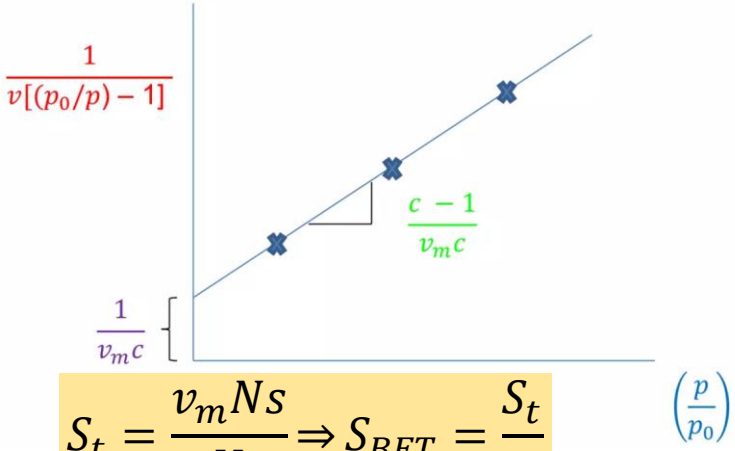


$$\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

$$v_m = \frac{1}{m+b}$$

$$y = mx + b$$

$$c = 1 + \frac{m}{b}$$



$$S_t = \frac{v_m N s}{V} \Rightarrow S_{BET} = \frac{S_t}{a}$$

v : adsorbed gas quantity
p_0 : saturation pressure of adsorbate
p : equilibrium pressure of adsorbate
c : BET constant = exp $[(E_1\text{-}E_L)/(RT)]$
E_1 : heat of adsorption for the first layer
E_L : heat of vaporization

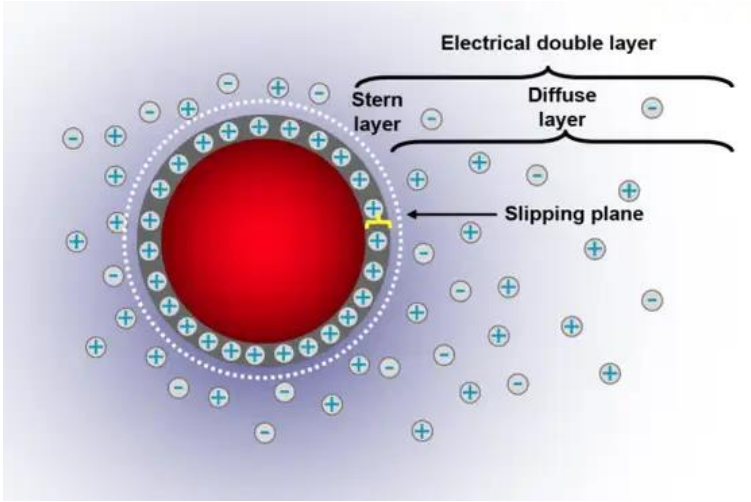
$$\frac{1}{v[\left(\frac{p_0}{p}\right)-1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

S_t : total surface area of material
v_m : monolayer adsorbed gas volume
N : Avogadro's number
s : cross-sectional area of adsorbed gas molecule
V : volume of adsorbed gas
a : mass of sample

Surface characterization

Shape | Size | Aggregation | Crystallinity | Chemistry | SSA | **S charge**

- Zeta potential
  - Suspension of NPs
  - Not the surface charge (electrical double layer)
  - Highly dependent on your medium
    - ionic strength and temperature



Henry equation

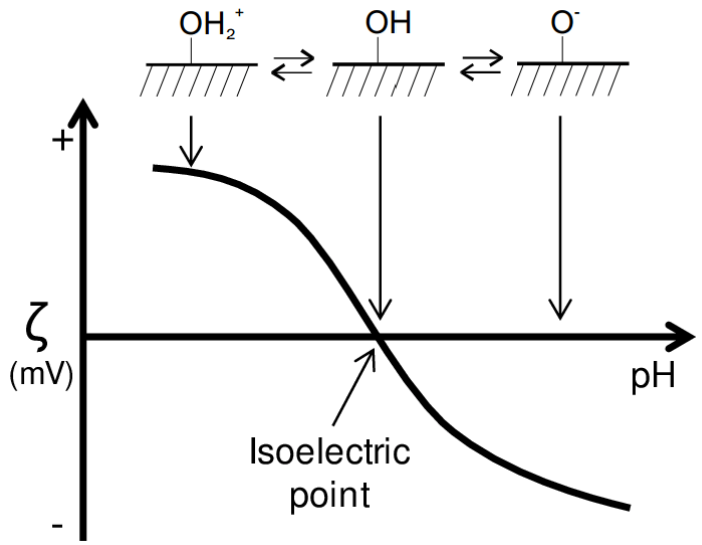
$$U_e = \frac{2\varepsilon z f(\kappa a)}{3\eta}$$ $f(\kappa a)$depends on temperature and ionic strength

U_e : electrophoretic mobility
ε : dielectric constant
z : Zeta potential
η : viscosity of dispersant
$f(\kappa a)$: Henry function

Surface characterization

- Zeta potential
  - Suspension of NPs
  - Not the surface charge (electrical double layer)
  - Highly dependent on your medium
    - Isoelectric point: pH where ZP = 0 mV

    → pH (mandatory to give results)



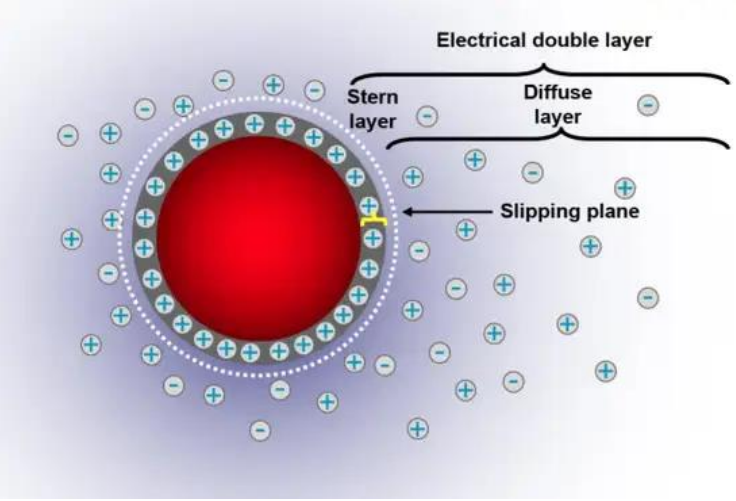
OXIDE MATERIAL	pH of IEP
Vanadium Oxide	1.5
Silicon Dioxide	2
Manganese Dioxide	3
Titanium Dioxide (Anatase)	3.5
Zirconium Dioxide	4
Indium Tin Oxide	6
Titanium Dioxide (Rutile)	6.5
Chromium Oxide	7
Iron Oxide	8
Aluminum Oxide	9
Yttrium	9
Lead Oxide	10
Nickle Oxide	10
Cadmium Oxide	11
Magnesium Oxide	12

From Malvern Panalytical

Surface characterization

Zeta	
Pros	**Cons**
Easy to use	Not for too high ionic strength

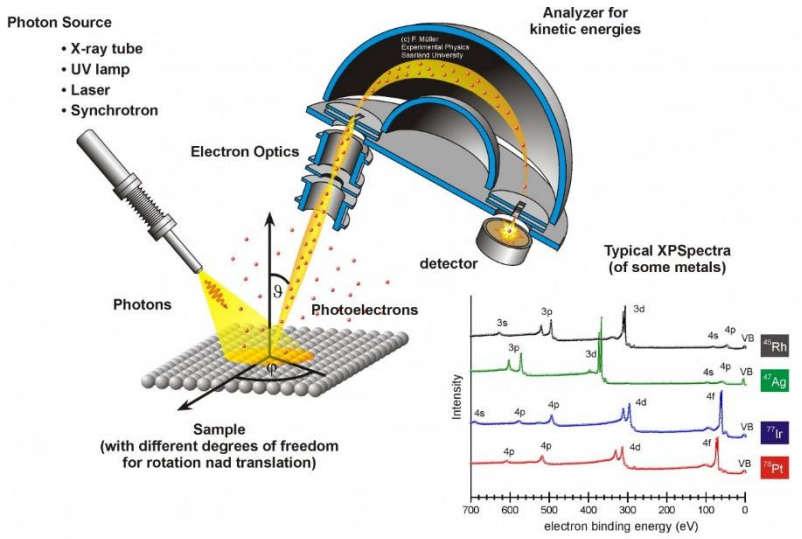
- Zeta potential
  - Suspension of NPs
  - Not the surface charge (electrical double layer)
  - Highly dependent on your suspension
    - Isoelectric point: pH where ZP = 0 mV
  - ”Stability” = f(Zeta) not totally correct

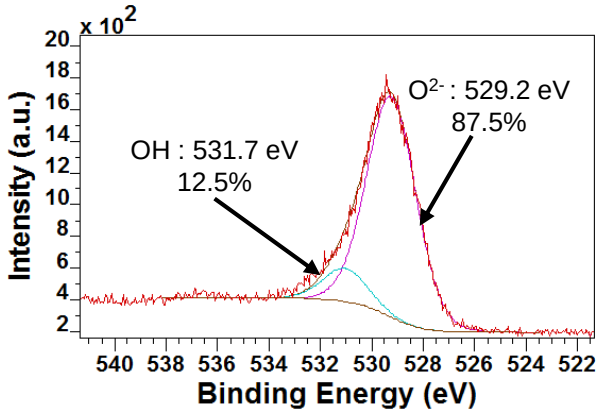


Zeta Potential (mV)	Stability
0 to ± 10	Highly unstable, rapid coagulation/flocculation
± 10 to 20	Limited stability
± 20 to 30	Moderately stable
> ± 30	Highly stable

Surface characterization

- XPS
  - Information on oxidation state
  - Organic molecules present (next lecture)





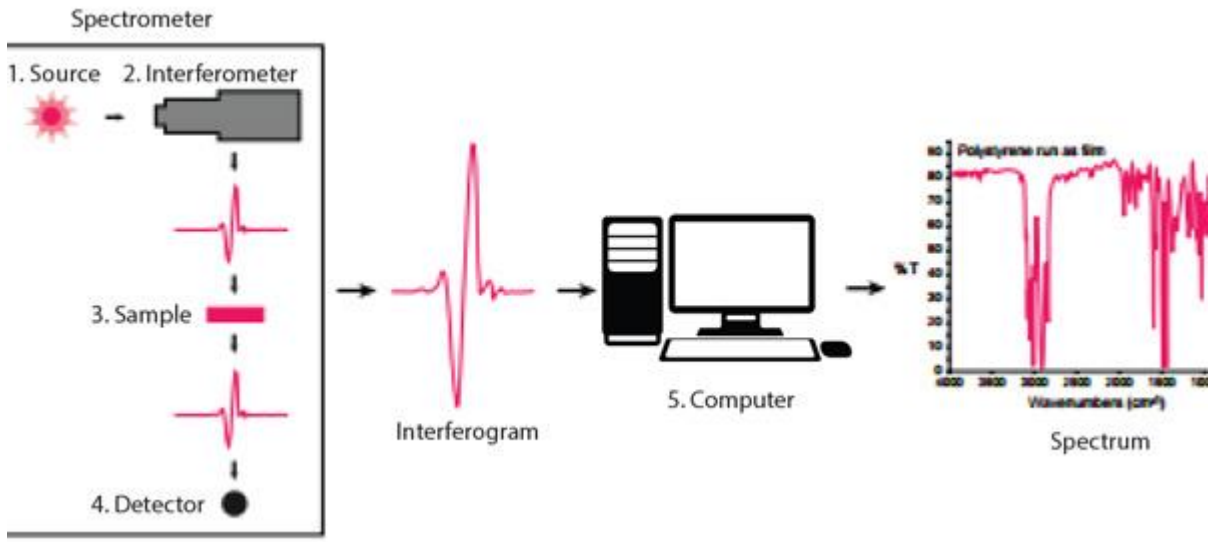
particles	Fe 2p (%)	O^{2-} (%)	OH (%)	C pollution (%)
Naked SPION	40	49	7	4

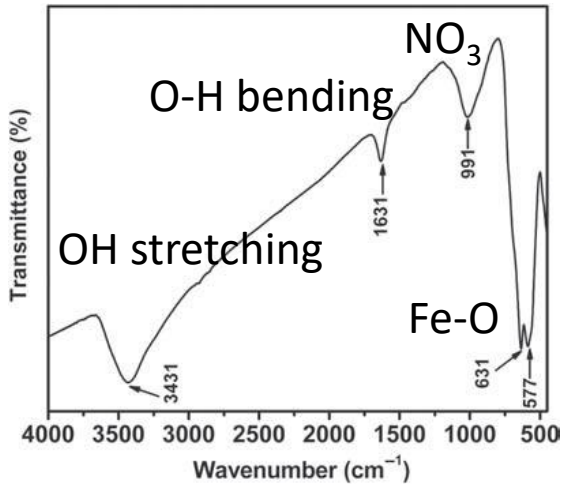
Hydroxyls groups at the surface of iron oxide NPs

Surface characterization

FTIR	
Pros	**Cons**
Easy to prepare and use	Need powder for inorganic
Fast	More for organic

- XPS
- FTIR Fourier transform infrared (FTIR) spectroscopy
  - 2-5 mg of powder in KBr pellet for inorganic material
  - Measure vibration of covalent bonds
    - More for organic compounds but can show presence of water and hydroxyl groups





https://doi.org/10.1166/SL.2014.3224

Surface characterization

Shape | Size | Aggregation | Crystallinity | Chemistry | SSA | S charge | **S chemistry**

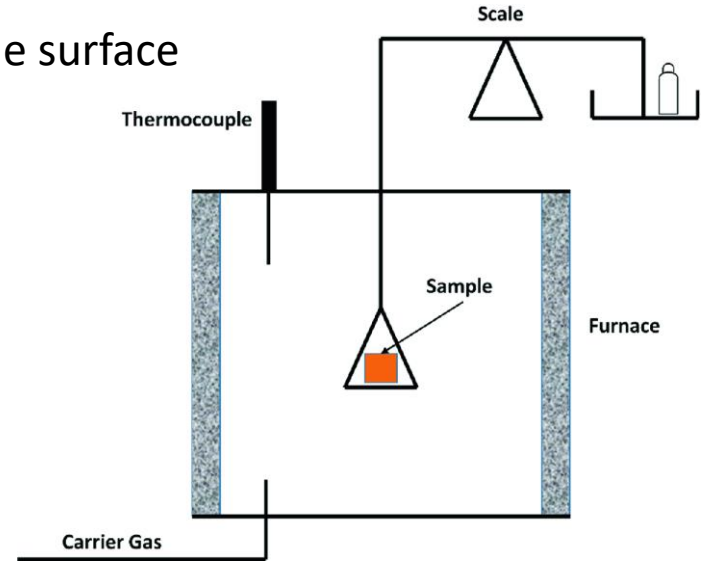
- XPS
- FTIR
- TGA Thermo-Gravimetric Analysis
  - 1-5 mg of powder
  - Scale in a furnace: Loss of mass = f(T)
  - More for organic but OH quantification possible

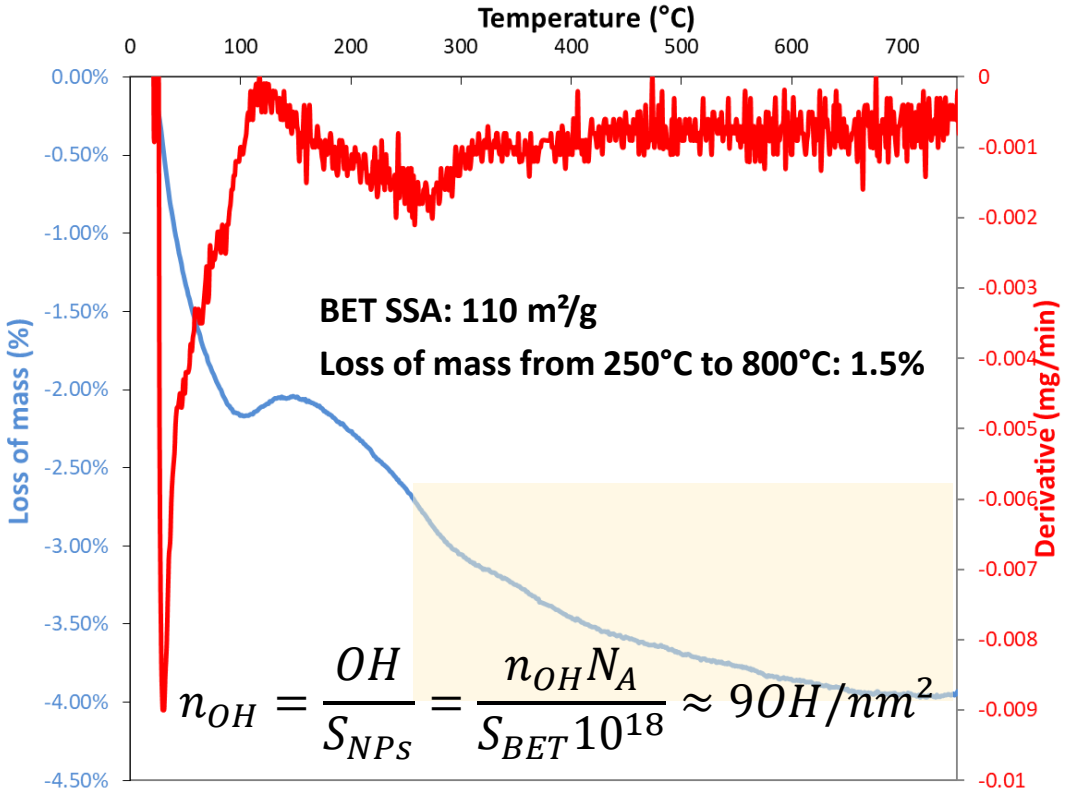
TGA	
Pros	**Cons**
Quantification of OH with BET	Destructive + organic

Equation linking TGA and OH on the surface of oxide NPs:

$$n_{OH} = 2n * H_2O = \frac{2\Delta m}{M_{H2O}}$$

n_{OH} : moles of OH per mass
Δm : loss of mass (%)
M_{H2O} : Molecular weight of H_2O



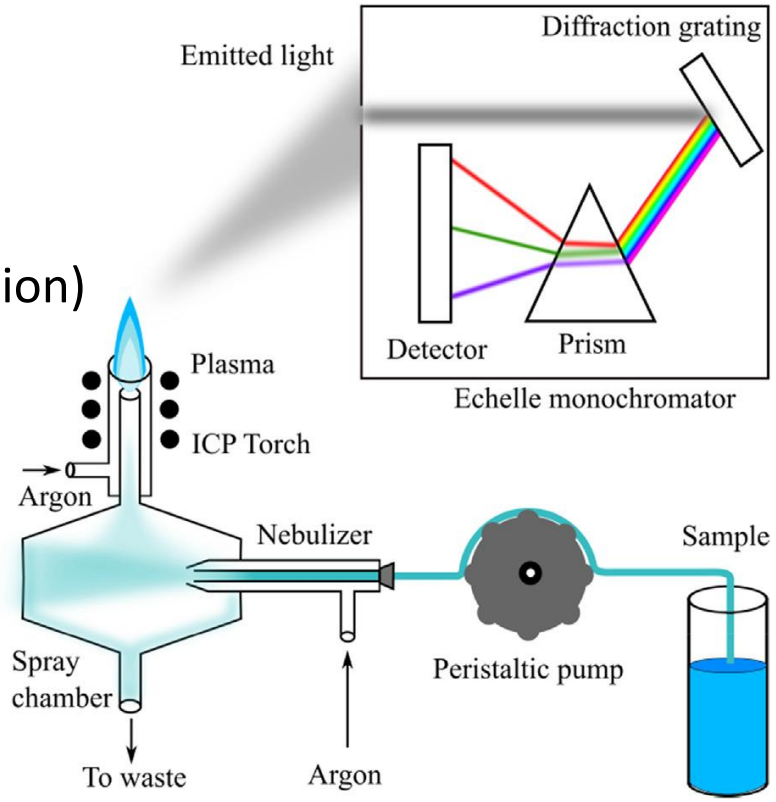


https://doi.org/10.1016/S0040-6031(01)00618-9

Solubility

- Solubility of inorganic NPs?
  - Rarely characterized
  - Dissolution of NPs in suspension?
- ICP
  - Analysis of solution of NPs (without dissolving NPs → destabilization)
  - Analysis at different times

  → important for biological studies especially toxicity



Summary

Shape → Size → Aggregation → Crystallinity → Chemistry → SSA → S charge → S chemistry → Solubility

ISO parameter	Techniques presented
Shape	TEM, SEM, AFM
Size (elementary)	TEM, SEM, AFM, XRD, SAXS, BET, UV-visible
Agglomeration	DLS, NTA, DCS
Crystallinity	XRD, TEM, SEM
Chemistry	XRD, TEM, SEM, XPS, ICP
Specific Surface Area	BET
Surface charge	Zeta potential
Surface chemistry	XPS, FTIR, TGA
Solubility	ICP

Techniques	Sample preparation / quantity[1]	Destructive?[2]
AFM	Powder on substrate (few mg)	Yes
BET	Powder ~10 m^2 (50-100 mg)	Yes
DCS	Suspension as such or diluted (100 µL)	Yes
DLS	Suspension as such or diluted (40 µL)	No
FTIR	Powder (2-5 mg) in KBr or Droplet	Yes or No
ICP	Suspension dissolved (ppm)	Yes
NTA	Suspension as such or diluted (100 µL)	No
SAXS	Suspension 10 µL at 1 mg/mL	No
SEM	Droplet of diluted sample or powder	Yes
TEM	Droplet (10 µL) of very diluted suspension	Yes
TGA	1-5 mg of powder	Yes
UV-Visible	Suspension as such or diluted 1mL	No
XPS	100 mg of powder	Yes
XRD	10th of mg of powder	Yes
ZETA	Suspension as such or diluted 1mL	No

Thank you!

[1] Quantity is sometimes difficult to estimate as it will depend on NPs parameters (size, color …)
[2] I assumed the technique is destructive if you have to dry powder or you change a parameter (T, vacuum…)

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