Oct. 22-23, 2007
Total scattering Pair Distribution Function analysis using X-rays and neutrons:
powder diffraction and complementary techniques
PDF Powder Diffraction Workshop at ESRF, Grenoble

Structural Analysis of Nano-Transition-Metal-Oxides

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Nano-Mn-oxide: Chemical Composition of a Gold Adsorbent

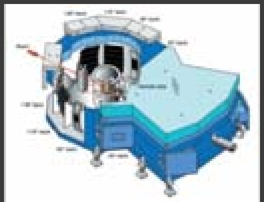
Summary

Introduction

High Intensity & High Resolution Total Scattering Diffractometers at Spallation Neutron Source Facilities

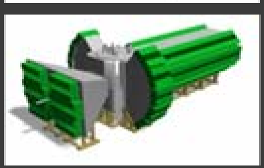
NPDF $\Delta Q/Q>0.15\%$

LANSCE L_1=32 m



iMATERIA $\Delta Q/Q>0.16\%$

JSNS (BL20) L_1=26.5 m

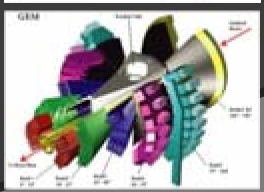


Versatile High Intensity Total Scattering Spectrometer

$\Delta Q/Q>0.25\%$ **JSNS (BL21)** L_1=15 m

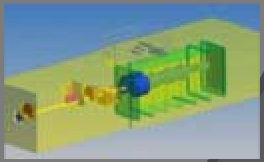
GEM $\Delta Q/Q>0.34\%$

ISIS L_1=17 m



NOMAD $\Delta Q/Q>0.25\%$

SNS L_1=19 m



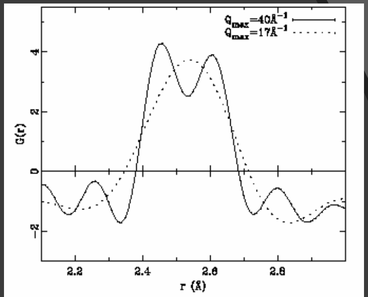
Fourier transformation

$S(Q) \longrightarrow G(r)$

***r*-resolution (Δr)**

Accessible highest *Q* (Q_{max})

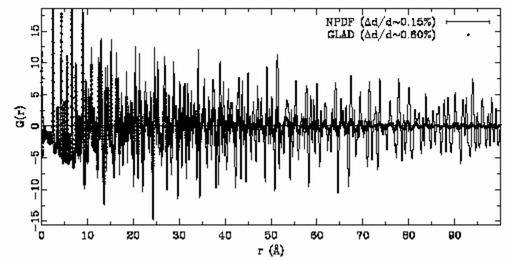
$$\Delta r \sim \pi / Q_{max}$$



Accessible highest *r* (r_{max})

***Q*-resolution (ΔQ)**

$$r_{max} \sim \pi / \Delta Q$$



S. Shamoto et al., KEK Report 16 (2001) 33 in Japanese.
Th. Proffen et al., Appl. Phys. A 74[Suppl.] (2002) S163-165.
X. Qiu et al., J. Appl. Cryst. 37 (2004) 110.

High Intensity & High Resolution

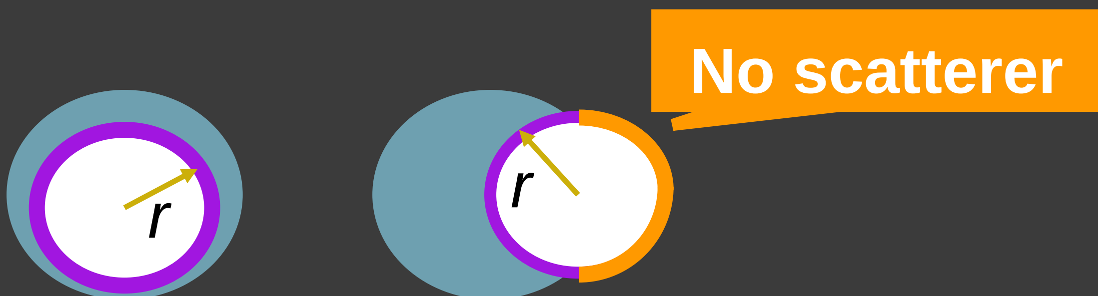
→ **Long scale structure with high *r*-resolution**

Nanoparticle structure

Finite size effects on PDF

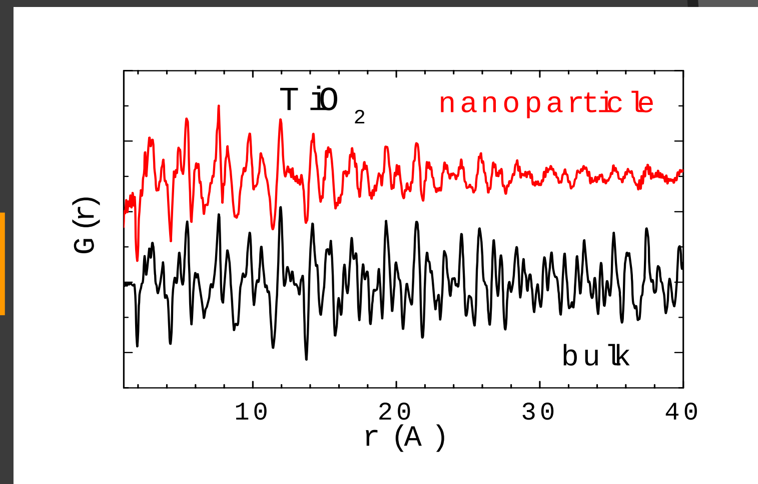
$$G(r) = \underbrace{f(r)G_\infty(r)}_{G_L(r)} + \underbrace{4\pi r(\rho_0' - \rho_0) f(r)}_{G_S(r)}$$

- **Small angle scattering**
- **Particle form factor**



Nanoparticle → *G*(*r*) is damped with increasing *r*.

NPDF (LANSCE)



"Finite Size Effects of Nanoparticles to the Atomic Pair Distribution Functions"
K. Kodama, S. Iikubo, T. Taguchi and S. Shamoto, Acta Cryst. A 62 (2006) 444-453 .

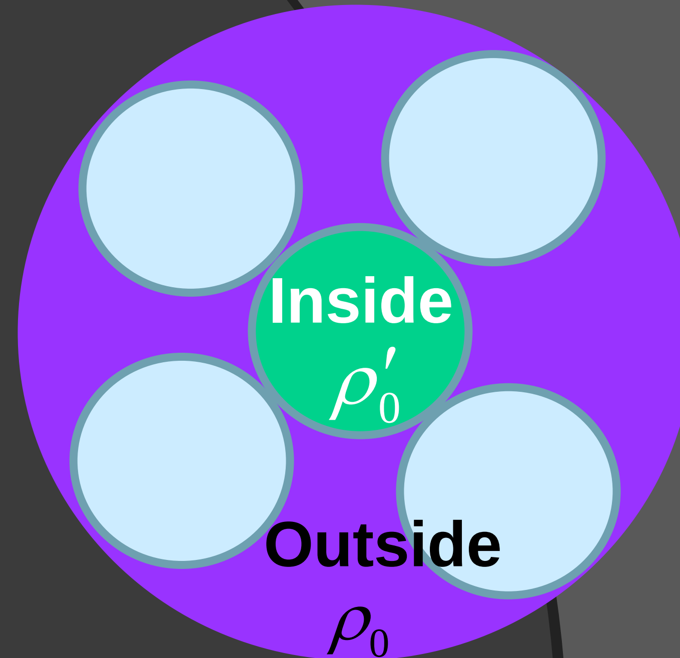
Small angle scattering

Inside **Outside**

$$\rho_0 g(r) = \underbrace{\rho_0' f(r) g_\infty(r)}_{\text{Inside}} + \underbrace{\rho_0 (1 - f(r)) g_{out}(r)}_{\text{Outside}}$$

$$g_{out}(r) = 1$$

$$= \rho_0' f(r)(g_\infty(r) - 1) + (\rho_0' - \rho_0) f(r) \cancel{+ \rho_0}$$



Outside is averaged as a mean field, leading to ρ_0.

$$S(Q) = 1 + \int_0^\infty 4\pi r^2 \rho_0 g(r) \frac{\sin(Qr)}{Qr} dr = S_L(Q) + S_S(Q) + \cancel{S(0)}$$

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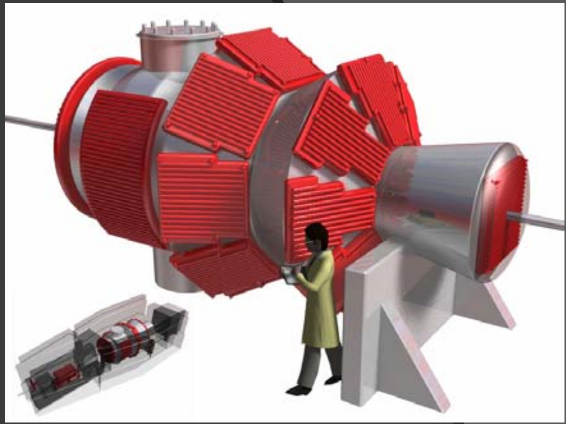
K. Kodama, S. Iikubo, T. Taguchi and S. Shamoto, Acta Cryst. A 62 (2006) 444-453 .

$$S_L(Q) = 1 + \frac{1}{Q}\int_0^\infty f(r)G_\infty(r)\sin(Qr)dr$$

$$S_S(Q) = \frac{1}{Q}\int_0^\infty 4\pi r(\rho_0' - \rho_0)f(r)\sin(Qr)dr$$



Versatile High Intensity Total Scattering Spectrometer in JSNS

$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S_L(Q) - 1 + S_S(Q)]\sin(Qr)dQ$$

$$= \underbrace{f(r)G_\infty(r)}_{G_L(r)} + \underbrace{4\pi r(\rho_0' - \rho_0)f(r)}_{G_S(r)}$$

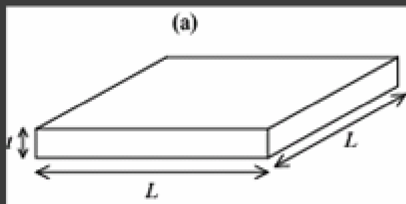
$$\approx f(r)G_\infty(r)$$

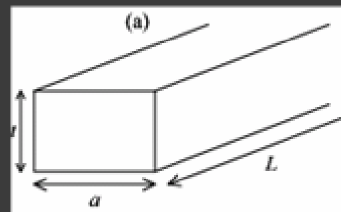
"Finite Size Effects of Nanoparticles to the Atomic Pair Distribution Functions"
K. Kodama, S. Iikubo, T. Taguchi and S. Shamoto, Acta Cryst. A 62 (2006) 444-453 .

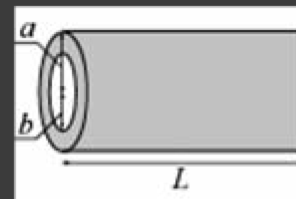
Particle form factor

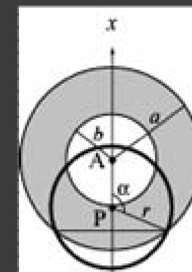
$G(r) \approx f(r) G_{\infty}(r)$ (Numerical Cal.)

Sheet | Belt | Rod & Tube | Sphere & Shell



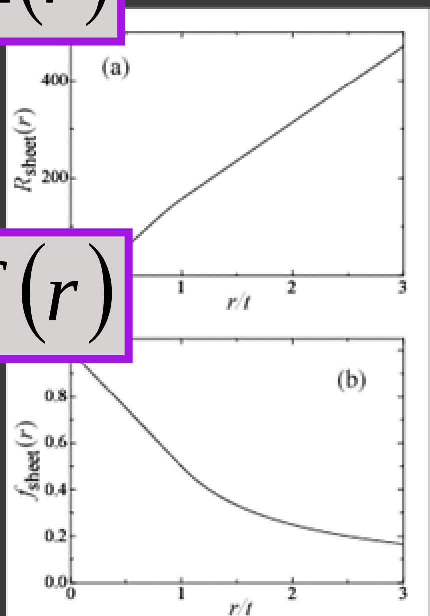


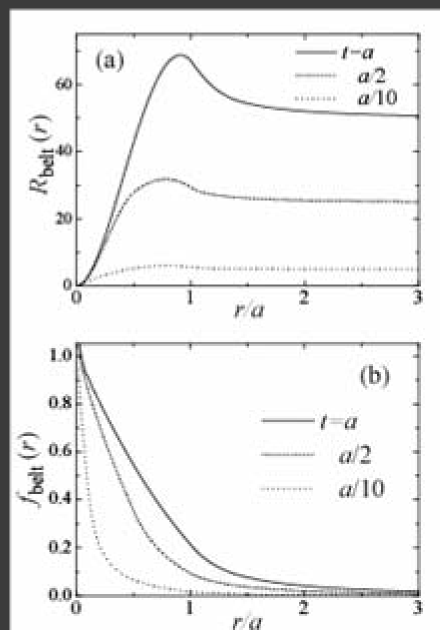


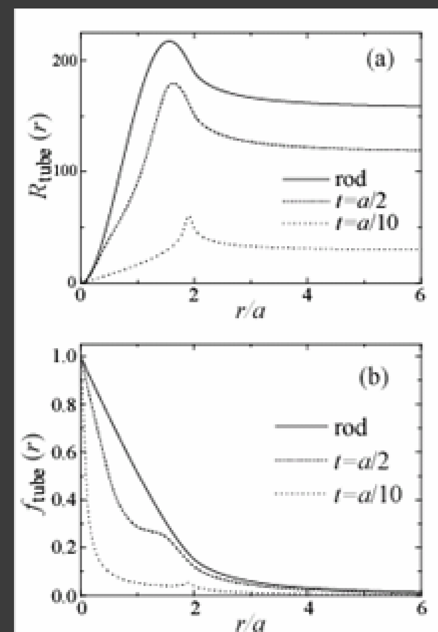


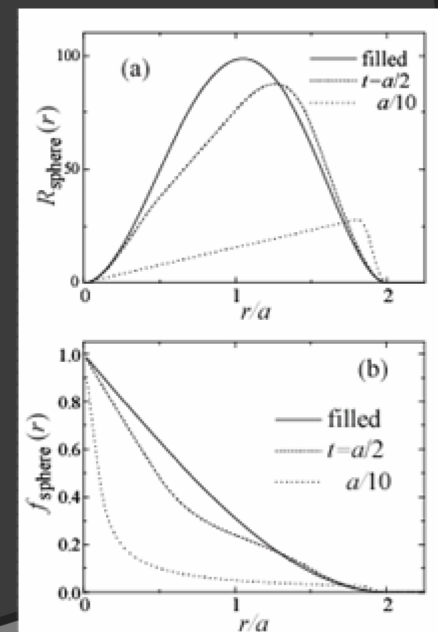
$R(r)$

$f(r)$







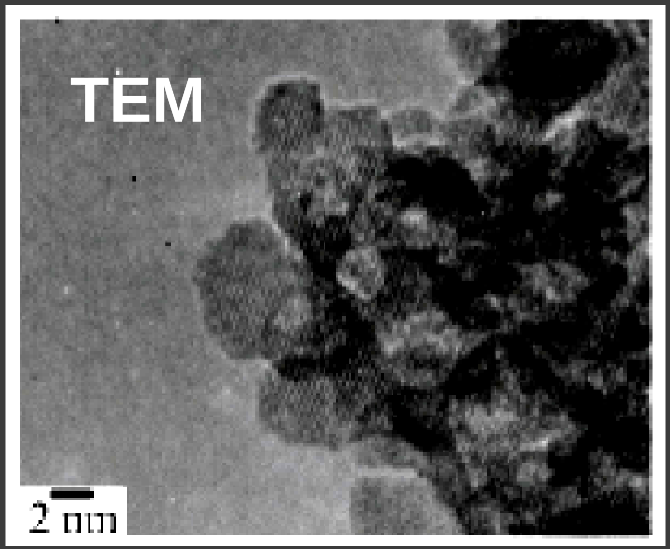


"Finite Size Effects of Nanoparticles to the Atomic Pair Distribution Functions"
K. Kodama, S. Iikubo, T. Taguchi and S. Shamoto, Acta Cryst. A 62 (2006) 444-453 .

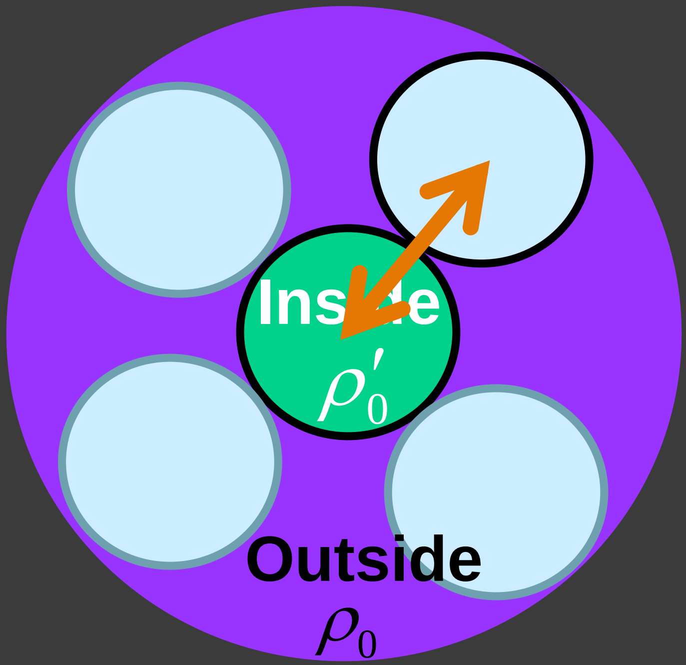
Research examples of nano-materials

Photo catalyst

TiO_2



TiO_2 nanoparticles

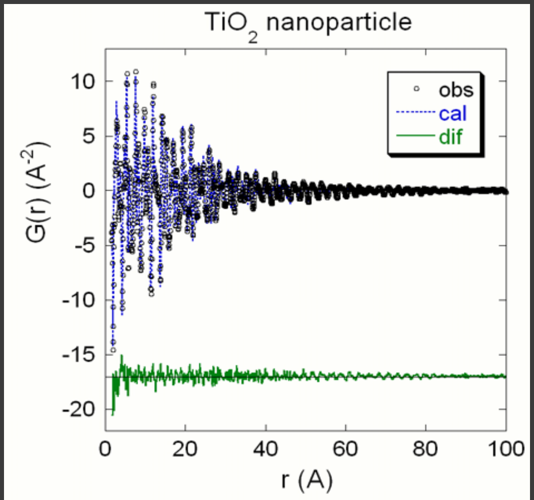


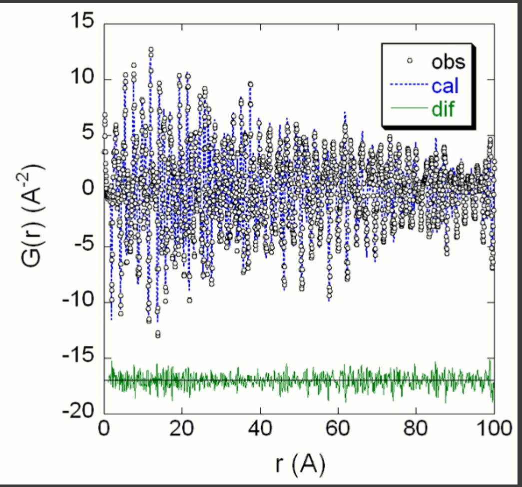
Particle pair correlation

Surface of nanoparticle

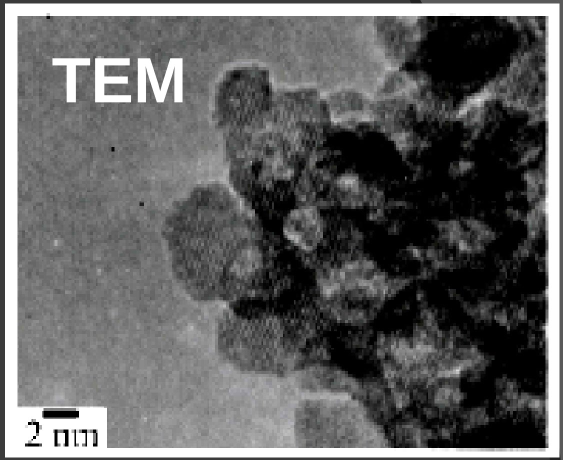
Aggregated nanoparticle

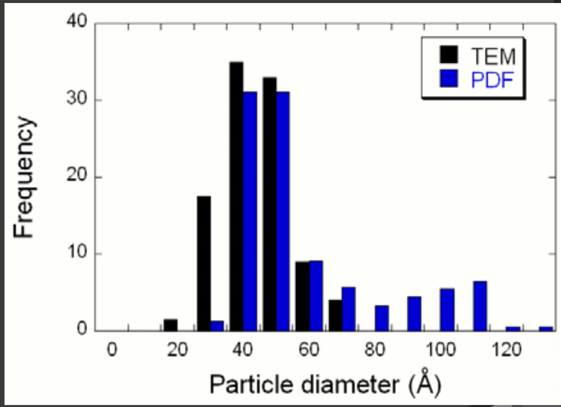
NPDF (LANSCE)





Nanoparticle **Crystalline**





Spherical particles with various diameters

$$G(r) = \sum_i N_i f_i(r) G_\infty(r)$$

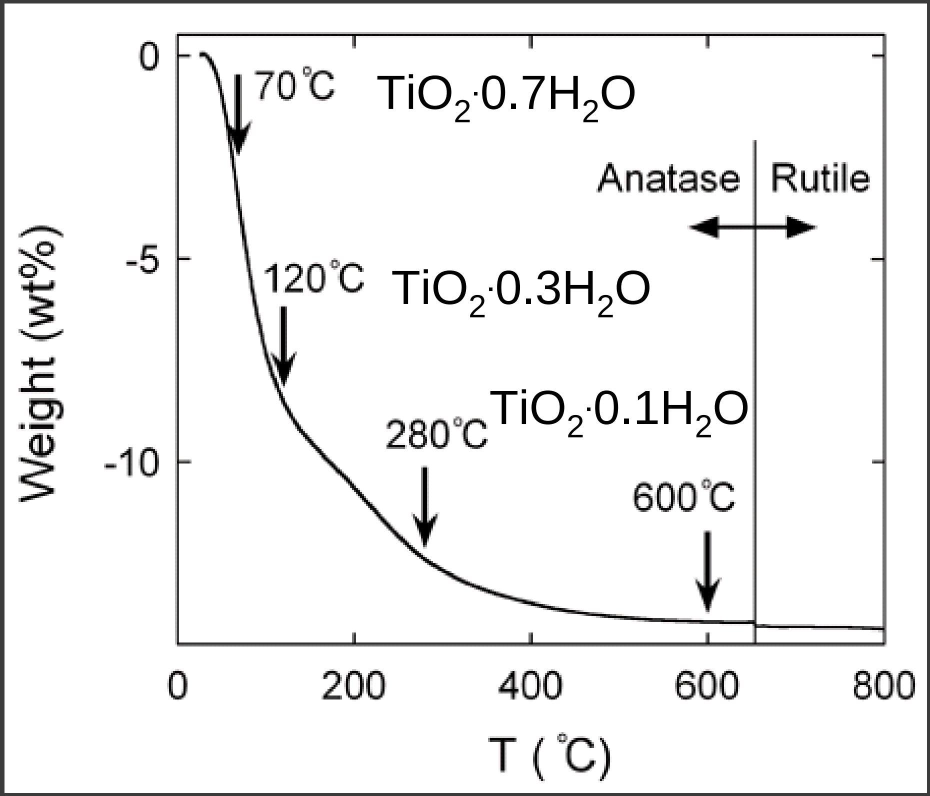
$$f_i(r) = \frac{1}{2}\left(\frac{r}{2a_i}\right)^3 - \frac{3r}{4a_i} + 1$$

No atomic correlation between particles

R_{wp}=18.4 %

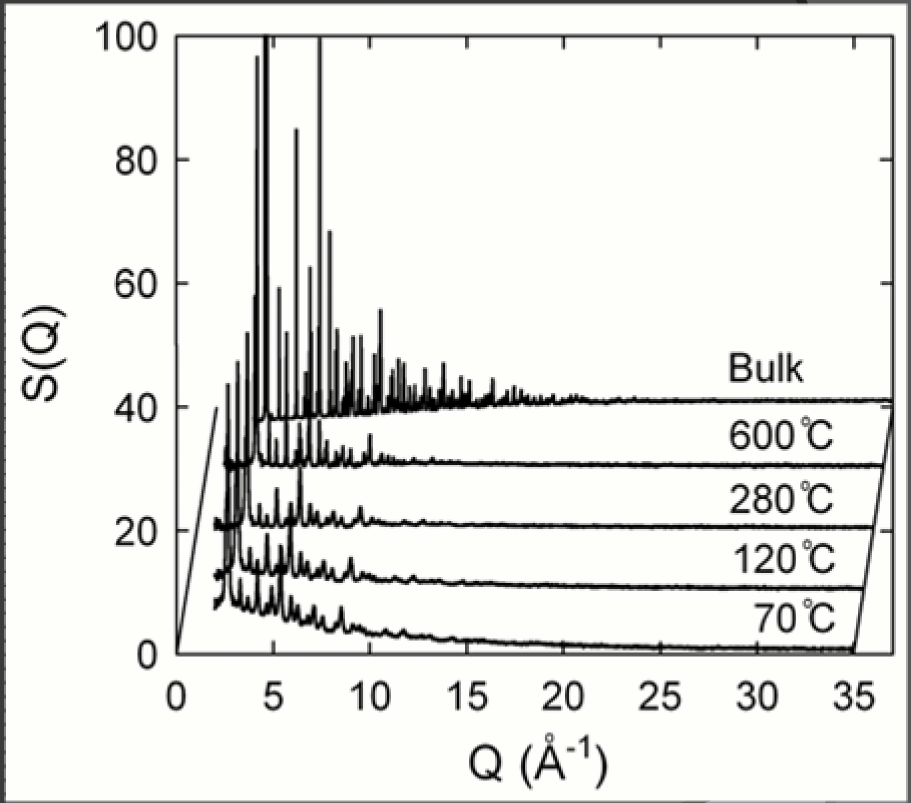
a=3.7921(4) Å^{-1}
c=9.477(3) Å^{-1}

With increasing temperature



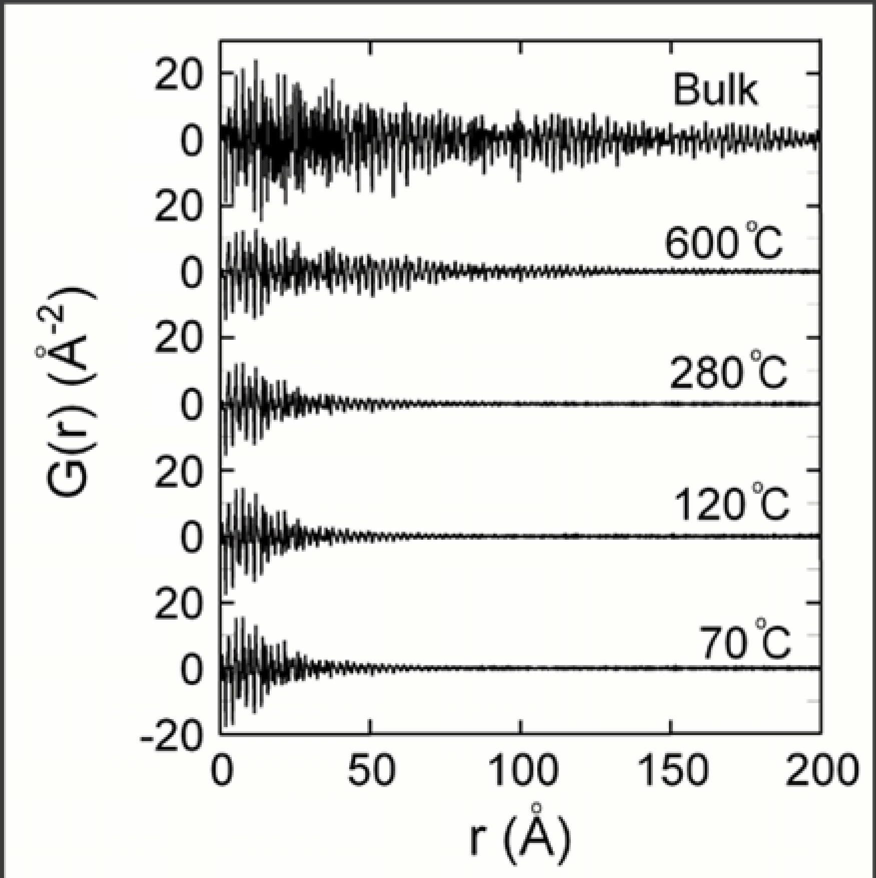
Thermal gravimetric analysis of TiO_2 nanoparticle sample.

NPDF (LANSCE)



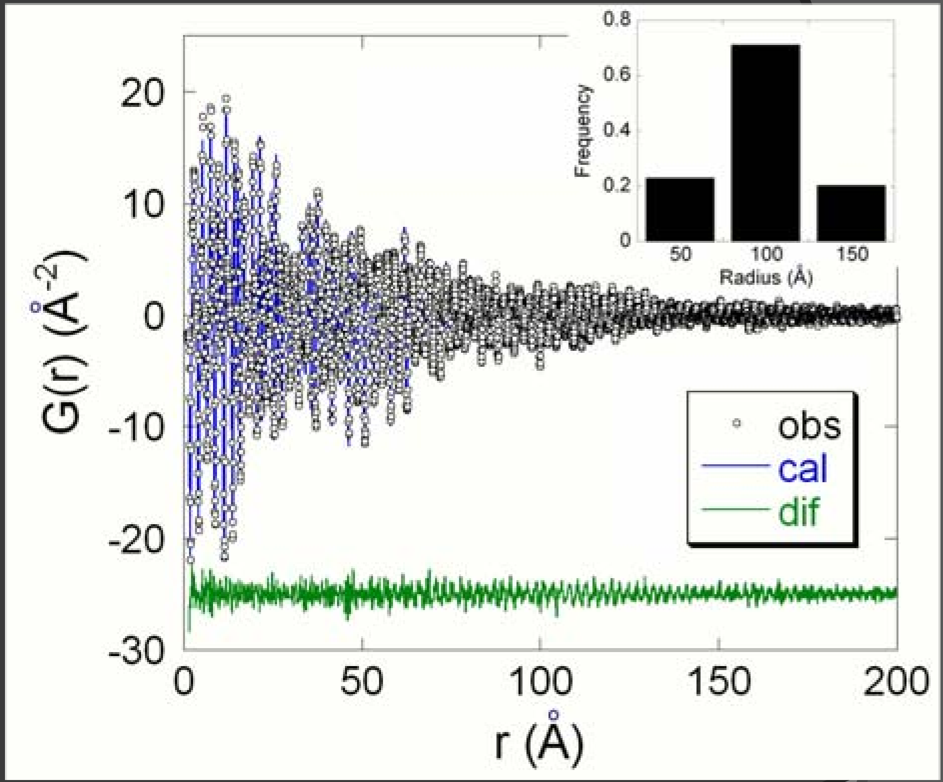
Structure functions of TiO_2 nanoparticle and bulk samples at various temperatures.

Surface dehydration of nanoparticle



PDFs at various temperatures.

NPDF (LANSCE)

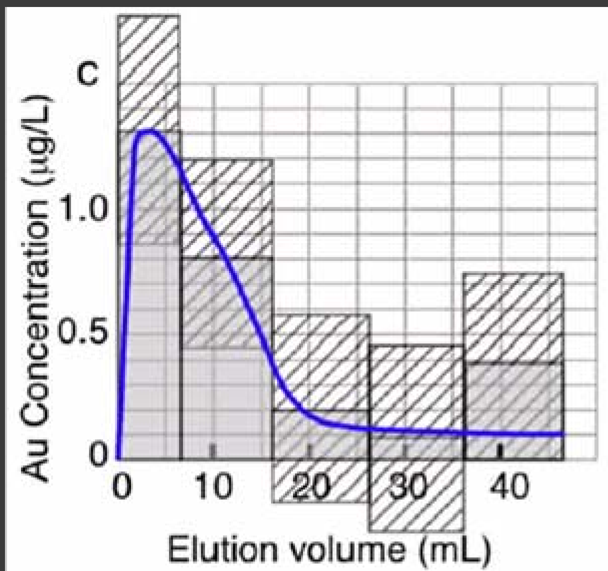


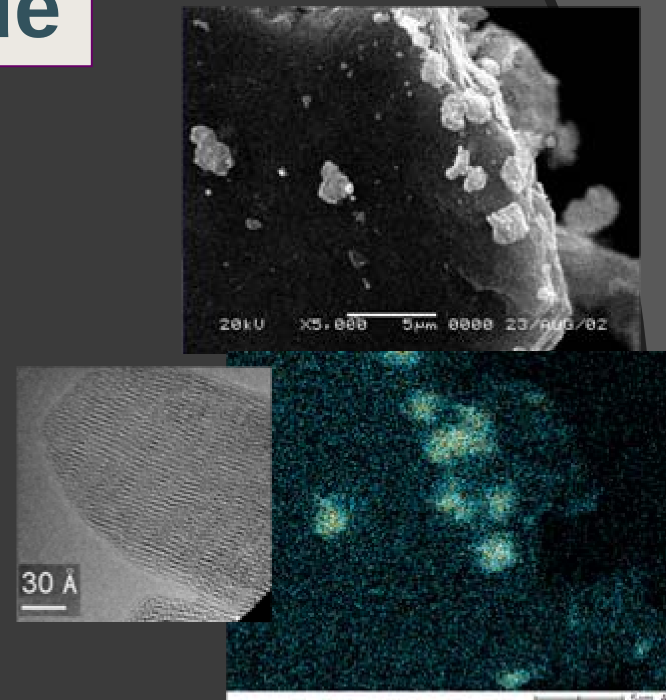
600 C data fitting R_{wp}=15.4%.

Only particle mean size increases!

Research examples of nano-materials

Gold adsorbent nano-Mn-oxide





1 ppt Gold 10 L Sea water, 10 g adsorbent,   3 days

19 ng gold extraction

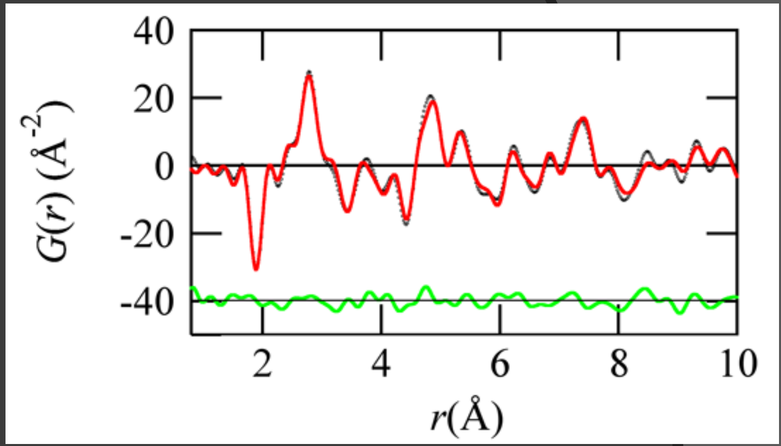
SEM & EDX images of grown gold particles on the adsorbent

Koyanaka, H.; Takeuchi, K.; Loong, C.-K. *Sep. Purif. Technol.* **2004**, *43*, 9.

Chemical composition of the nano-Mn-oxide

$$c_{\mathrm{Mn}} = \frac{1}{2}\frac{W\langle b\rangle^2}{n\left|b_{\mathrm{Mn}}b_{\mathrm{O}}\right|} = \frac{1}{1+x}$$

c_{Mn}: atomic fraction of manganese ion in MnO_x
W : integrated intensity of a RDF peak
n : the coordination number (CN) of a Mn ion.



NPDF (LANSCE)

$$2x = n\exp\left(\frac{l_0 - l_1}{B}\right)$$

l_0 and *B* are bond valence sum parameters
l_1 : the nearest neighbor bond length between transition metal and oxygen ions.

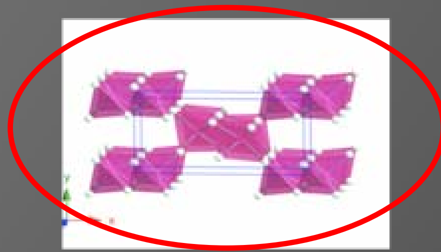
n=6 (C.N.)
c_{Mn}=0.33 ± 0.03 (Neutron), 0.327 ± 0.012 (X)
2*x* =3.91 ± 0.35 (Neutron), 3.85 ± 0.15 (X)
… $Mn^{+3.9}O_2$

→ **MnO_2**

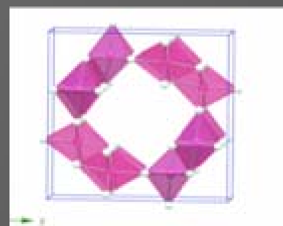
D. I. Brown, D. Altermatt, *Acta Cryst. B* **41**, 244, (1985).
S. Iikubo, H. Koyanaka, S. Shamoto, K. Takeuchi, S. Kohara, K. Kodama, C.-K. Loong, in preparation.

Crystal structure of the nano-Mn-oxide

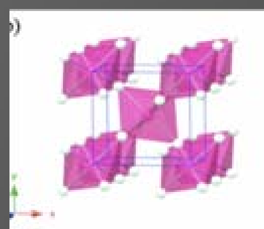
R-MnO_2



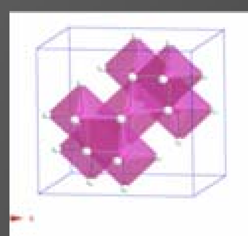
α-MnO_2

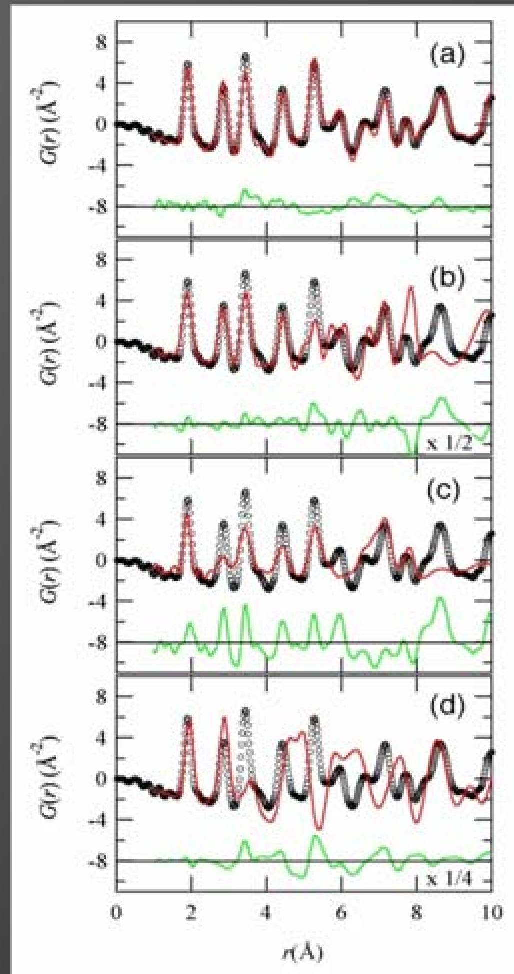


β-MnO_2

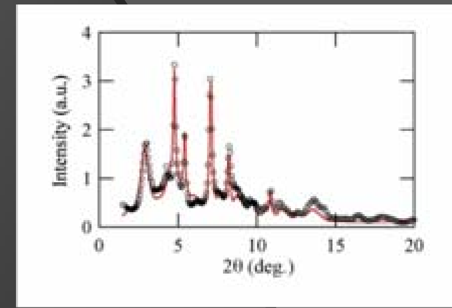


λ-MnO_2





Real Space



Reciprocal Space

BL04B2 beamline (SPring-8)
incident energy of 61.63 keV,
λ = 0.20118 Å

Summary

Finite size effects on PDF

Small angle scattering effect on

Particle form factor on PDF

Research examples of nano-materials

Nano-Ti-oxide	Surface crystal water/Hydroxyl group randomly occupy surface sites
Nano-Mn-oxide	Chemical composition and Crystal structure

A picture is worth 1000 words.

A workshop is worth 1000 papers.

SABAC2008

January 10-11, 2008, Tokai, Japan

International Workshop on Structural Analyses Bridging over between Amorphous and Crystalline Materials

http://nsrc.tokai-sc.jaea.go.jp/sabac/

IUCr

2008, Osaka, Japan