ISSN: 2633-4828 Vol. 5 No.4, December, 2023

International Journal of Applied Engineering & Technology

DETERMINATION OF SIZES OF FE_3O_4 NANOPARTICLES: RESULTS OF COMPARATIVE X-RAY DIFFRACTION (XRD) ANDSMALL ANGLE X-RAY SCATTERING (SAXS) STUDIES

Swapnil S Sagare[1a], P.S. Goyal[2b], Sundeep H Deulkar[1c], Deepali Shrivastava[3d*], Ashwani Kumar[4e] and Debasis Sen[4, 5f]

[1]Department of Physics, Pillai College of Engineering, New Panvel- 410206, India
[2]Department of Electronics and Computer Science, Pillai College of Engineering, NewPanvel- 410206, India
[3]Department of Chemistry, Pillai College of Engineering, New Panvel- 410206, India
[4]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India
[5] Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, India
[a]swapnilsagare912@gmail.com [b]psgoyal@mes.ac.in, [c]saisundeep@mes.ac.in, [d]deepali@mes.ac.in, [e]debasis@barc.gov.in and [f]ashwanikumar@rrcat.gov.in

ABSTRACT

X-ray Diffraction is a standard method for determining the sizes of nanoparticles. However, this method does not give size distributions of particles if there is a polydispersityin particle sizes. XRD provides an average size for the particles. Small Angle X-ray Scattering (SAXS) is another technique for determining the sizes of nanoparticles. This technique provides not only mean size but also size distribution of particles. This paper reports the results of XRD and SAXS experiments on indigenously synthesized Fe_3O_4 nanoparticles.

Keywords: Nanoparticles, Iron Oxide, Size Distribution, XRD, SAXS

1. INTRODUCTION

Nanoparticles are particles of organic or inorganic materials having sizes in the range of 1–100 nm [1-3]. In general, these particles could be made of crystalline materials (e.g., metals, Fe_3O_4) or amorphous materials (e.g., polymers). The nanoparticles are usually coated with a suitable surfactant or a polymer (referred to as capping) to stabilize them against aggregation [2, 3]. The physical properties of nanoparticles depend on their sizes. For example, the color of a gold nanoparticle depends on its size [5]. The size of a nanoparticle is, again, an important parameter when it comes to its use in industry [6,7], biotechnology [8], or medicine [9]. It is thus of interest to determine the sizes of nanoparticles. Scanning Electron Microscope (SEM) [10], Transmission Electron Microscope (TEM) [11], X-ray diffraction (XRD) [12], Dynamic Light Scattering (DLS) [13], Small Angle X-ray scattering (SAXS) [14 - 16] and Small Angle Neutron Scattering (SANS) [15 - 17] are some of the techniques which have been used for determining sizes of nanoparticles. These techniques have their merits and demerits. For example, TEM provides a direct image of the particle over a wide range of sizes. However, it does not provide statistically averaged information as the technique involves using very small samples. Moreover, sample preparation for TEM is a specialized job and most of the users find it difficult to use TEM. XRD is much simple and user-friendly technique, but can be used for crystalline materials only. However, it does not provide information about the shape of the particle. SAXS and SANS are better suited for determining, both, the sizes, and shapes of nanoparticles. The technique involves using bulk-size samples and thus it provides statistically averaged quantitative information about the sizes and shapes of nanoparticles. This paper deals with the use of XRD and SAXS in the study of nanoparticles. At times, a combined SAXS and SANS study can be exploited to get a detailed structure of the particle. For example, it has been used for studying the core-shell structure of nanoparticles [18, 19]. In particular, the sizes of Fe_3O_4 nanoparticles as obtained using XRD and those obtained using SAXS are compared. The measurements have been made on three sets of Fe_3O_4 particles differing in their capping materials; these particles were synthesized in our laboratory.

2. SALIENT FEATURES OF NANOPARTICLES OF FE_3O_4

Iron oxide, Fe_3O_4, is a crystalline material that exhibits magnetic properties and is known as magnetite in the literature. It is often used in the synthesis of ferrofluids, which find applications in industry, biotechnology, and medicine [20]. To avoid self-agglomeration of Fe_3O_4 particles, they are coated with a suitable surfactant or

polymer. Fe_3O_4 particles, having three different coatings, were synthesized using the co-precipitation technique. The details of starting materials and the method of synthesis are given in an earlier paper [21, 22]. Three sets of Fe_3O_4 particles were synthesized; the coating material was PEG for Set-I, CA for Set-II, and OA for Set-III. It may be mentioned that the choice of the coating material is an important parameterin deciding the suitability of the above particles for a specific application [23]. Results of XRD and SAXS studies on the above nanoparticles are reported in Sections 3 and 4 respectively.

3. X-RAY DIFFRACTION STUDIES ON FE_3O_4 NANOPARTICLES

X-ray diffraction is a standard method for determining the microscopic structure of materials [12, 24]. The experiment involves the scattering of a monochromatic beam of X-rays (wavelength =λ) by the sample and recording the angular distribution of scattered X-rays using a suitable detector. The measured plot between scattered intensity and the scattering angle (2θ) is referred to as an x-ray diffraction pattern. X-ray diffraction patterns for three sets of Fe_3O_4 particles were recorded at UGC DAE CSR, Mumbai Centre, BARC, Mumbai using a commercial diffractometer (Bruker D2 Phase 2nd Gen Diffractometer having XE-T detector). X-rays having wavelength λ = 0.154 nm (Cu-Kα X-rays) were used. Data were recorded in steps of 0.02° for 2θ in the range of 10° -70°.

Figure 1 shows the measured XRD patterns for the three samples. They show well-defined (220), (311), (400), (422), (511), (440), (620), and (533) Bragg peaks in agreement with the standard Fe_3O_4 powder diffraction data [ICSD-158741]. The average values of lattice constants for PEG-coated, OA-coated, and CA-coated nanoparticles of Fe_3O_4, as obtained from the above peaks, are 0.832 nm, 0.837 nm, and 0.835 nm respectively and they are in reasonable agreement with the value of 0.838 nm, reported in the literature [24].

The importance of XRD studies in the present contest lies in the fact that sizes of nanoparticles can be obtained from the widths of Bragg peaks. It is known that the Bragg peak is very sharp (δ- function) for a macroscopic particle and its width increases as the particle size decreases [25].

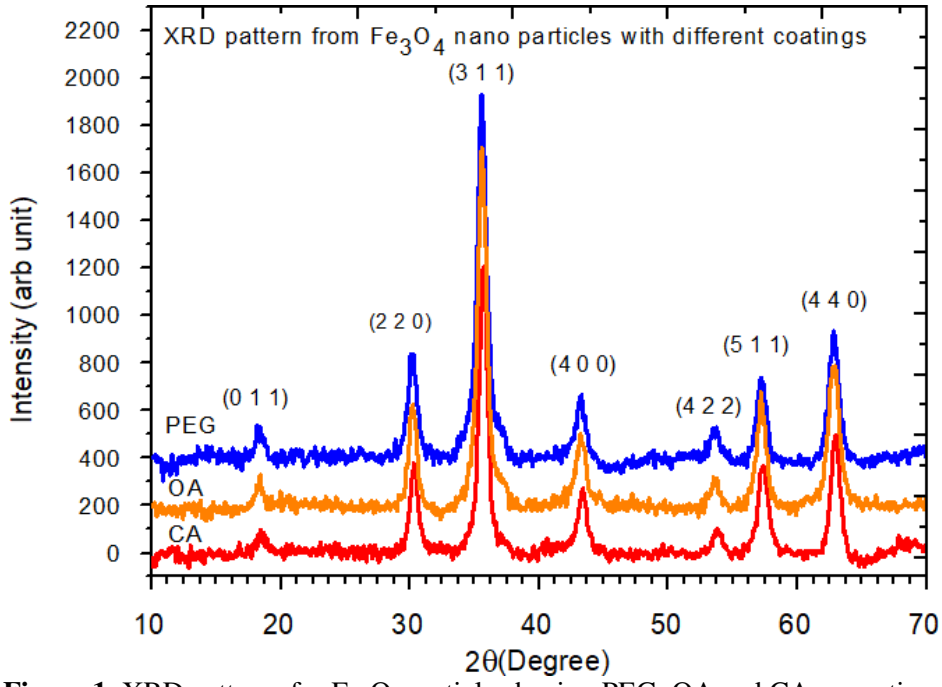

Figure 1. XRD patterns for Fe_3O_4 particles having PEG, OA and CA as coatings

The particle sizes were calculated by measuring the half-height widths of the strongest reflection (i.e., 311) and using the well-known Debye-Scherrer formula [25, 26]

$D_{XRD} = 0.75\ L$ (1)

Here D_{XRD} is the diameter of the particle and L is the coherent length for a spherical particle and is given by

$L = 0.94\ \lambda/\beta\cos(\theta)$ (2)

where β is full width at half maximum (in radians) of the peak. The values of calculated sizesfor the three samples are given in Table 1.

4. SAXS STUDIES ON Fe_3O_4 NANOPARTICLES

4.1 Introduction to Small Angle X-ray Scattering (SAXS)

Small Angle X-ray Scattering (SAXS) is a somewhat specialized technique and it is not surprising that SAXS machines are available in advanced laboratories only. It is thus appropriate to give a small introduction to the technique. SAXS is a technique for studying the structure of materials on mesoscopic length scales. The importance of this technique lies in the fact that it provides information that is not easily available from other techniques. For example, SAXS is used to determine the sizes and shapes of biological molecules suspended in biological fluids, information that cannot be obtained using conventional techniques such as TEM, XRD, etc. [15]

SAXS experiment and XRD experiments are similar, in the sense that both involve the scattering of a monochromatic beam of x-rays (wavelength = λ ~ 0.1 nm) by the sample and measuring the scattered x-ray intensity as a function scattering angle (2θ). The differences lie in the range of 2θ. Scattering angles are less than 5^o for SAXS experiments and much larger (in the range of 10^o to 100^o) for XRD experiments. Difficulty in performing the SAXS experiment arises from the fact that the incident beam spills over and gives rise to a background at small angles and that interferes with the scattered signal. SAXS experiment measures scattered intensity as a function of the wave vector transfer Q (= 4π sin θ / λ). The wave vector transfer Q for SAXS is much smaller (0.005to 0.20 nm^{-1}) as compared to that for (~ 5 nm^{-1}) for XRD. That is, unlike conventional diffraction experiments, where the structure of a material is examined at atomic resolution (~0.2 nm), SAXS is used for studying the structure of a material with a spatial resolution of ~ 5 nm. SAXS is thus used for studying the sizes of nanoparticles having sizes in the range of 1 nm to 100 nm. The importance of SAXS emerges from the fact that it can be used not only for determining the sizes but also the shapes of nanoparticles. In the case of polydisperse samples, SAXS is used to obtain information about the size distributions of nanoparticles. More importantly, while XRD is used for crystalline materials, SAXS can be used for, both,crystalline and amorphous materials.

4.2 Results of SAXS Experiments on Fe_3O_4 Nanoparticles

SAXS experiments have been carried out on three samples, namely, PEG-coated Fe_3O_4 nanoparticles, CA-coated Fe_3O_4 nanoparticles, and OA-coated Fe_3O_4 nanoparticles. Measurements were carried out on a state-of-the-art SAXS beamline at the Indus-2 synchrotron, Raja Ramana Centre for Advanced Technology (RRCAT) [27], Indore. This machine operates on beamline BL-18 of an indigenously built synchrotron (Indus-2), which provides an intense beam of X-rays. The said SAXS beamline uses a double crystal monochromator, pin-hole geometry, and a two-dimensional online image plate detector for detecting scattered X-rays. During the present experiments, 16 KeV x-rays (wavelength = 0.0775 nm) and sample-to-detector distance were kept at 3.239 m. Radial averaging was performed on 2D data, using standard procedures [27], to obtain a variation of scattering intensity with Q. Fig.2 shows measured SAXS profiles for Fe_3O_4 nanoparticles having coatings of PEG, CA, and OA.

4.3 Analysis of SAXS data from Fe_3O_4 nanoparticles

SAXS data were analyzed using SASfit software [28] under the assumption that the sample consists of spherical particles of varying sizes. This assumption is reasonable as TEM studies on similar Fe_3O_4 nanoparticles showed that particles are nearly spherical and have polydispersity in size [21]. The scattered x-ray intensity I (Q) for the above situation is givenby [27]

$$I(Q) = n(\Delta\rho)^2 \int P(Q, R)\, D(R)\, V^2(r)\, dR \quad (3)$$

where P (Q, R) is the particle form factor and D(R) is the particle size distribution function. In general, the particle form factor depends on the size and shape of the particle. The form factor for a spherical particle of radius R is given by:

$$P(Q, R) = [3\{\sin(Q R) - (Q R)\cos(Q R)\} / (Q R)^3]^2 \quad (4)$$

The expression of log-normal size distribution is written as follows:

$$D(R) = \exp(-[\ln(R/R_0)]^2 / 2\sigma^2) / [\sqrt{((2\pi \sigma^2 R^2)}] \quad (5)$$

where "R_0" and "σ" denote the median radius and the polydispersity index of the size distribution, respectively. V(R) is the volume of the particle having radius R. The scattered intensity depends on the product of number density (n) and contrast factor ($\Delta\rho^2$). The diameters of particles can be obtained from median radii using the following equation

$$D_{SAXS} = 2 R_0 \exp(\{\sigma^2\}/2) \quad (6)$$

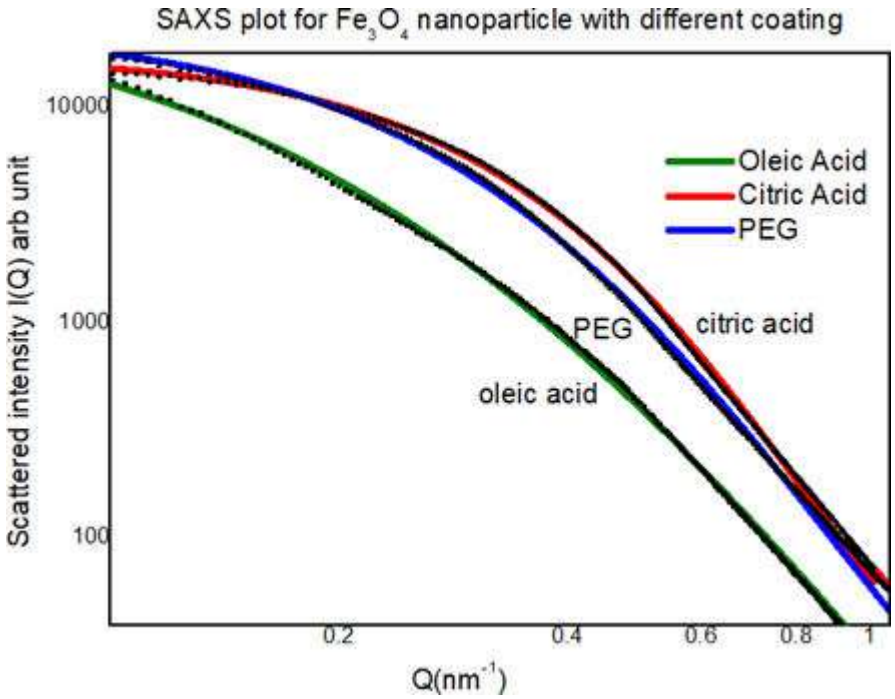

Figure 2. Measured SAXS distributions for Fe_3O_4 nanoparticles having PEG, CA, and OA coatings. Solid lines are least square fits as discussed in the text.

The solid lines in Fig. 2 are SASfit-based nonlinear least square fits of Eq.3 to the measured scattering intensities with R_0, σ, and normalizing constant as fitting parameters. The values of the fitted parameters are given in Table 1. The size distributions of PEG, CA, and OA-coated Fe_3O_4 nanoparticles were obtained using Eq. 5 and the above-fitted parameters of the three sets of data. It is noted that the values of median radii for the above three samples are 3.16 nm, 3.63 nm, and 1.75 nm respectively. For the sake of comparison, SAXS values for the diameters (D_{SAXS}) of the particles are given in Table 1. It is seen that the sizes of PEG-coated Fe_3O_4 nanoparticles and CA-coated Fe_3O_4 nanoparticles are similar for XRD and SAXS. However, the diameter of OA-coated Fe_3O_4 nanoparticles obtained using SAXS is much smaller than that obtained using XRD. The reasons for these differences are not clear. It may be mentioned that at times SAXS experiments measure the size of the grain and XRD experiments measure the size of coherent crystallite. This could not be the reason as D_{SAXS} is smaller than D_{XRD} for OA-coated nanoparticles. We believe that the present experiments, both XRD and SAXS, measure crystallite sizes for PEG, CA, and OA-coated Fe_3O_4 nanoparticles.

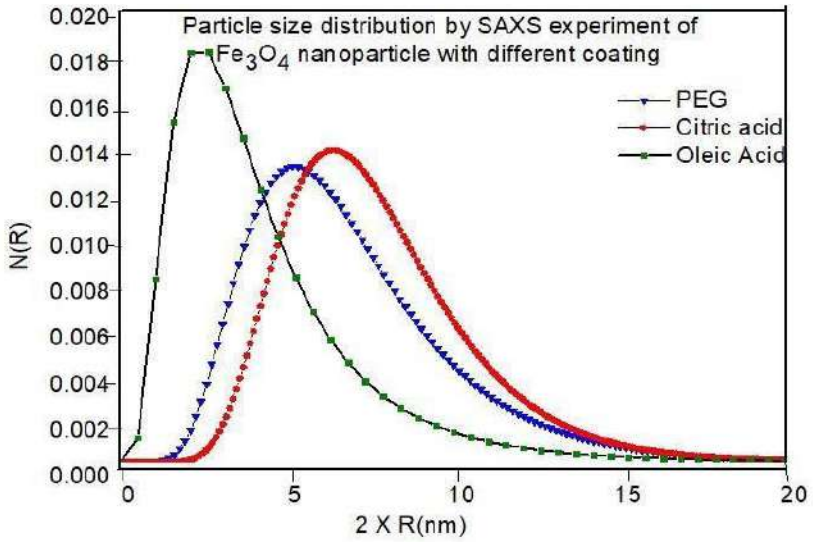

Figure 3: Size distributions of Fe_3O_4 nanoparticles having three different coatingsas obtained from SAXS data.

Table 1. Sizes of Fe_3O_4 nanoparticles having three different coatings as obtained fromSAXS and XRD

Sr no	Fe3O4 nanoparticles Having coating of	Fitted parameters (using SASfit)			Particle diameter usingSAXS D_{SAXS} = 2 R_0 exp ({σ^2}/2) (nm)	Particle diameter using XRD D_{XRD} (nm)
		n	σ	R_0 (nm)		
1	PEG	0.044	0.43	3.16	6.88	5.70
2	Oleic acid	0.04	0.62	1.75	3.81	6.03
3	Citric acid	0.045	0.35	3.63	7.91	7.51

SUMMARY

It is of interest to study the sizes, polydispersity, and shapes of nanoparticles as they are the most important parameters in deciding their usefulness in industry or biotechnology. A variety of experimental techniques have been used for the above. The choice of technique depends on several parameters such as whether the constituent material of the nanoparticle is crystalline or amorphous, and the presence or absence of polydispersity in sizes and shapes. It is seen that different techniques, often, give different values for the size parameters. This paper deals with the comparison of xrd and saxs in determining the sizes of nanoparticles. Xrd and saxs studies were carried out on three samples, namely, polyethylene glycol (peg) coated fe3o4 nanoparticles, citric acid (ca) coated fe3o4 nanoparticles and oleic acid (oa) coated fe3o4 nanoparticles. The nanoparticles were synthesized in our laboratory using the wet coprecipitation technique. Xrd experiments were carried out using a conventional x-ray diffractometer and saxs experiments were carried out using a state-of-the-art saxs machine in a synchrotron source. The mean sizes of the above nanoparticles were obtained from xrd data by analyzing the widths of bragg peaks and using of debye scherrer method. Saxs data were analyzed in terms of a model that assumed the sample consisted of polydisperse spherical nanoparticles. The size distributions of nanoparticles were obtained by analyzing saxs data using the standard software (sasfit). It is seen that both techniques give similar values (~ 7 nm) for the mean sizes of peg-coated fe3o4 nanoparticles and ca-coated fe3o4 nanoparticles. This is not the case for oleic acid-coated fe3o4 nanoparticles. The mean size (dxrd = 6.03 nm) of oa-coated fe3o4 nanoparticles as obtained using xrd, is much larger than that (dsaxs = 3.8) obtained using saxs. The reasons for these differences are not clear.

REFERENCES

1. C. N. R. Rao, A Muller and A K Cheetham (2004), Nanomaterials – An Introduction, in C N.R. Rao et al., (Eds.), The Chemistry of Nanomaterials, Wiley-VCH, Verlag,Singapore.
2. Sulabha K Kulkarni, Nanotechnology: Principles and Practices, Springer, 2014
3. A. Nouilhat (2006), An Introduction to Nanoscience and Nanotechnology, John Wiley & Sons, USA.
4. Chi M Phan and Hoang M Nguyen, Role of capping in wet synthesis of nanoparticles,J Phys, Chem. A 121 (2017) 3213
5. A N Gadge, S J Wadhar and A D Landge, Gold nanoparticles, International Journal of Science and Healthcare Research 5 (2020) 21
6. K Raj, B Moskowitz, and R Casciari, Advances in ferrofluid technology, J, Magn. Magn. Mater. 149 (1995) 174
7. P John and J M Laskar, Optical Properties and applications of ferrofluids-A Review, J. Nanofluids 1 (2012) 3
8. A Akbarzadeh, M Samiei and S Davaran, Magnetic nanoparticles: preparation, physical properties, and applications in biomedicine, Nanoscale Research Lett. 7 (2012) 144
9. K Wu, D Q Su, J M Liu, R Saha and J P Wang, Magnetic nanoparticles in nanomedicine: a review of recent advances, Nanotechnology 30 (2019) 502003
10. V D Hodoroaba et.al., Characterization of nanoparticles by means of high-resolution SEM, IOP Conf. Series: Materials Science and Engineering 109 (2016) 012006
11. D H Anjum, "Characterization of nanoparticles with transmission electron microscope, IOP Conf. Series: Materials Science and Engineering 146 (2016) 012001
12. B.D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publishers, California,1978.
13. Zaman, M., Characterizing nanoparticle size by dynamic light scattering technique,Graduate Thesis and Dissertations, University of Arkansas, Fayette, 2014.
14. O. Glatter and O. Kratky, Small Angle X-Ray Scattering, Academic Press, New York, 1982
15. Jill Trewhella, Recent advances in small-angle scattering and its expanding impact in structural biology, Structure 30 (2022) 215
16. L. A. Feigin and D. J. Svergun (1987), Small angle X-ray and Neutron Scattering, PlenumPress, New York.
17. Cy M Jeffries, Z Pietras, and D I Svergun, "The basics of small-angle neutron scattering", The European Physical Journal Conferences 236 (2020) 03001
18. V K Aswal, P S Goyal, H Amenitsch and S. Bernstoff, Counter ion condensation in ionic micelles as studied by a combined use of SAN and SAX, Pramana J. Phys. 63 (2004) 333
19. P S Goyal and V K Aswal, Use of SANS and SAXS in the study of nanoparticles, International Journal of Nanoscience 5 (2005) 987.
20. R V Mehta, Synthesis of magnetic nanoparticles and their dispersions with special reference to applications in biomedicine and biotechnology, Materials Science and Engineering C 79, (2017) 90
21. B Panda and P S Goyal, "Oleic acid-coated magnetic nanoparticles: Synthesis and characterization" AIP Conference Proceedings 1665 (2015) 050020

22. Bhakti Hirani et al. (2023), "Magnetic Properties of Fe_3O_4 Nanoparticles having several different coatings, Accepted for publication in Bull. Materials Science.
23. U Klekotka, D Satuła, A Basa and B Kalska-Szostko, Importance of surfactant quantity and quality on growth of iron oxide nanoparticles, Materials 13, (2020) 1747
24. N Nakagiri, M H Manghnani, L C Ming and S Kimura, Crystal structure of magnetite under pressure, Physics, and Chemistry of Minerals 13, (1986) 238
25. S Mustapha et al., Synthesis and characterization of TiO_2 nanoparticles: X-ray peak profile analysis using Williamson–Hall and Debye–Scherrer methods, International Nano Letters 11, (2021) 241
26. J. Nanda, B.A. Kuruvilla and D.D. Sarma, Photoelectron spectroscopy of CdS nanocrystallites, Phys. Rev. B 59, (1999) 7443
27. A Das, J Bahadur, A Kumar and D Sen, Performance of small and wide-angle x-ray scattering beamline at indus-2 synchrotron, Rev. Sci. Inst. 94, (2023) .43902
28. J Kohlbrecher (2018), SASfit: A program for fitting simple structural models to small-angle scattering data, A Manual of Paul Scherrer Institute, Switzerland.