



High pressure induced atomic and mesoscale phase behaviors of one-dimensional TiO₂ anatase nanocrystals

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Impact statement

The high pressure behavior of nanocrystals (NCs) continues to be of interest, as previous studies have demonstrated that an externally applied pressure can serve as an efficient tool to induce structural phase transitions of NC assemblies at both the atomic scale and mesoscale without altering any chemistry by manipulating NC interatomic and interparticle distances. In addition, the high pressure generated deviatoric stress has been proven to be able to force adjacent NCs to connect and fuse into new crystalline nanostructures. Although the atomic structural evolution of TiO₂ NCs under pressure has been widely investigated in the past decades, open questions remain regarding the mesoscale phase transition and morphology of TiO₂ NC assemblies as a function of pressure. Therefore, in this work, systemic high pressure experiments on ordered arrays of TiO₂ nanorods and nanorices were conducted by employing wide/small angle x-ray scattering techniques. The sintering of TiO₂ assemblies at mesoscale into various nanostructures under pressure were revealed by transmission electron microscopy. Overall, this high pressure work fills the current gap in research on the mesoscale phase behavior of TiO₂ assemblies. The observed morphology tunability attained by applying pressure opens new pathways for engineering nanomaterials and optimizing their collective properties through mechanical compression stresses.

Here, we report the high pressure phase and morphology behavior of ordered anatase titanium dioxide (TiO₂) nanocrystal arrays. One-dimensional TiO₂ nanorods and nanorices were synthesized and self-assembled into ordered mesostructures. Their phase and morphological transitions at both atomic scale and mesoscale under pressure were studied using *in situ* synchrotron wide- and small-angle x-ray scattering (WAXS and SAXS) techniques. At the atomic scale, synchrotron WAXS reveals a pressure-induced irreversible amorphization up to 35 GPa in both samples but with different onset pressures. On the mesoscale, no clear phase transformations were observed up to 20 GPa by synchrotron SAXS. Intriguingly, sintering of TiO₂ nanorods at mesoscale into nano-squares or nano-rectangles, as well as nanorices into nanowires, were observed for the first time by transmission electron microscopy. Such pressure-induced nanoparticle phase-amorphization and morphological changes provide valuable insights for design and engineering structurally stable nanomaterials.

Introduction

In recent years, high pressure-induced atomic phase transition of titanium dioxide (TiO₂) nanocrystals (NCs) has been intensively investigated and demonstrated to be dependent on both the crystal size and morphology.^{1–3} Among the four commonly known polymorphs of TiO₂ (i.e., anatase, rutile, brookite, and TiO₂-B), anatase TiO₂

NCs have been the most widely studied phase due to its significantly different phase transition pathways compared to the bulk as well as the noticeable nano-confinement effects. Bulk anatase TiO₂ transforms from tetragonal to an orthorhombic α -PbO₂ phase at $\sim$ 2–5 GPa, and then to the monoclinic baddeleyite phase at $\sim$ 12–15 GPa;⁴

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while in the case of TiO₂ anatase NCs, besides the increased phase transition pressure, they also display three different transition pathways depending on the particle size: (1) transition to amorphous phase for particles below 10 nm; (2) transition directly to baddeleyite phase for particles in the size range of 12–50 nm; and (3) similar phase transitions as that of the bulk materials for particles larger than 50 nm.^{5,6} Furthermore, the shape of NC has also been found to play a key role in determining the high pressure behaviors of TiO₂ NCs. For example, shape-dependent compressibility in anatase TiO₂ NCs has been studied by Park et al.;⁷ high pressure-induced amorphization has been reported for TiO₂-B nanoribbons by Li et al.;⁸ a direct anatase to baddeleyite phase transition for TiO₂ nanowires has been observed by different groups.^{9,10} Moreover, nanostructured anatase TiO₂ with diverse morphology and composition, such as TiO₂ nanotubes,^{11,12} TiO₂ NCs with curved surfaces,¹³ metal doped TiO₂ NCs,¹⁴ TiO₂ 2D nanosheets,^{15,16} and nanoporous TiO₂ materials¹⁷ have all been reported under pressure and have shown discrete high pressure behaviors.

On the other hand, compression of NC ordered arrays at the mesoscale has been found to result in sintering of neighbor NCs leading to morphological changes and new nanostructures.² To date, pressure has been proven to be a powerful tool in tuning the mesoscale structures as well as the morphology of various NC assemblies.^{18–23} However, previous high pressure experimental studies on TiO₂ NCs focused mainly on their atomic scale phase transitions. The high pressure behaviors of self-assembled mesoscale arrays of TiO₂ NCs have not been studied in detail and are poorly understood.

Therefore, in this work, ordered arrays of anatase 1D TiO₂ NCs were studied under pressure for the first time, using *in situ* synchrotron small- and wide-angle x-ray scattering (SAXS/WAXS) techniques combined with diamond anvil cells (DACs). We have investigated 1D TiO₂ NCs of different shapes, namely, nanorods and nanorices. We report here that the on-site pressure of atomic phase amorphization is dependent on the particle size and shape, while no mesoscale structural transition is observed for either sample. In addition, we demonstrate by transmission electron microscopy (TEM) that high pressure treatment can effectively manipulate characteristics of NC superlattices and connect 1D TiO₂ NCs into different nanostructures.

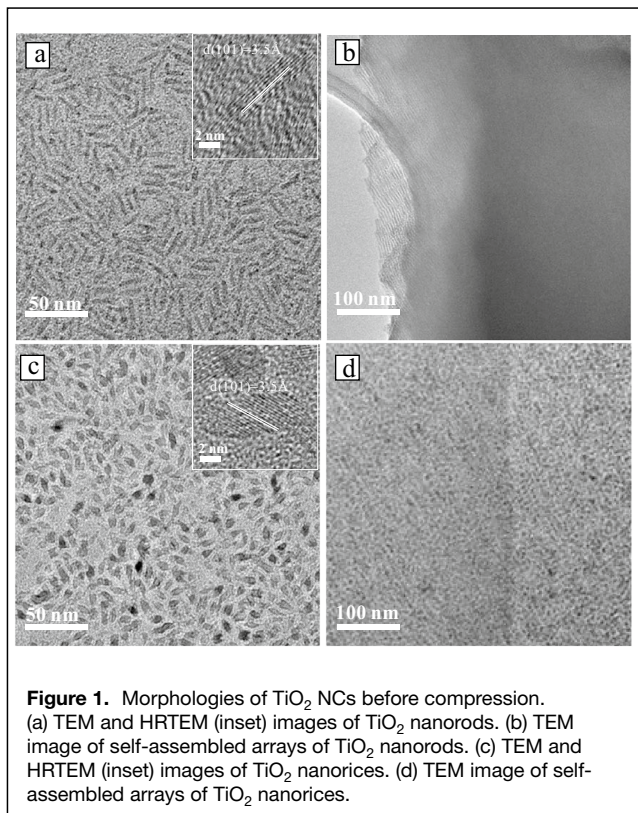
Results and discussion

TiO₂ NCs were synthesized using previously reported solution phase synthesis methods with slight modifications (Supplementary Information (SI)).^{24,25} TEM images of as-synthesized nanorods and nanorices are shown in **Figure 1a**, c. The diameter and length of nanorods are 2.8 ± 0.4 nm and 18.7 ± 2.2 nm, respectively; and, for nanorices, are 4.1 ± 0.5 nm and 9.2 ± 0.8 nm, respectively. From high-resolution TEM (HRTEM) images (insets in **Figure 1a**, c), the *d*-spacing of lattice fringes of both samples are ~ 3.5 Å, which corresponds to the (101) plane of anatase crystal structure. Ordered TiO₂ NC arrays were fabricated by drop-casting

corresponding toluene solutions onto silicon wafers, followed by slow drying under ambient conditions. The dried NC thin films were scraped off, analyzed by TEM directly and loaded into DACs for high pressure studies (An overview of the experimental procedure is shown in the schematic diagram in **Figure S1**, SI). The TEM images of the edge of the ordered NC arrays are shown in **Figure 1b**, d.

At ambient conditions, the WAXS patterns of TiO₂ nanorods and nanorices were measured and the tetragonal anatase structures for both NCs are confirmed (**Figure S2**, SI). The calculated lattice parameters are summarized in Table S1, which closely match those observed for the bulk anatase TiO₂.²⁶ SAXS patterns collected at ambient conditions show that nanorods are packed into a 2D hexagonal mesophase and nanorices are assembled into a face-centered cubic (fcc) mesophase (**Figure S3**, SI).

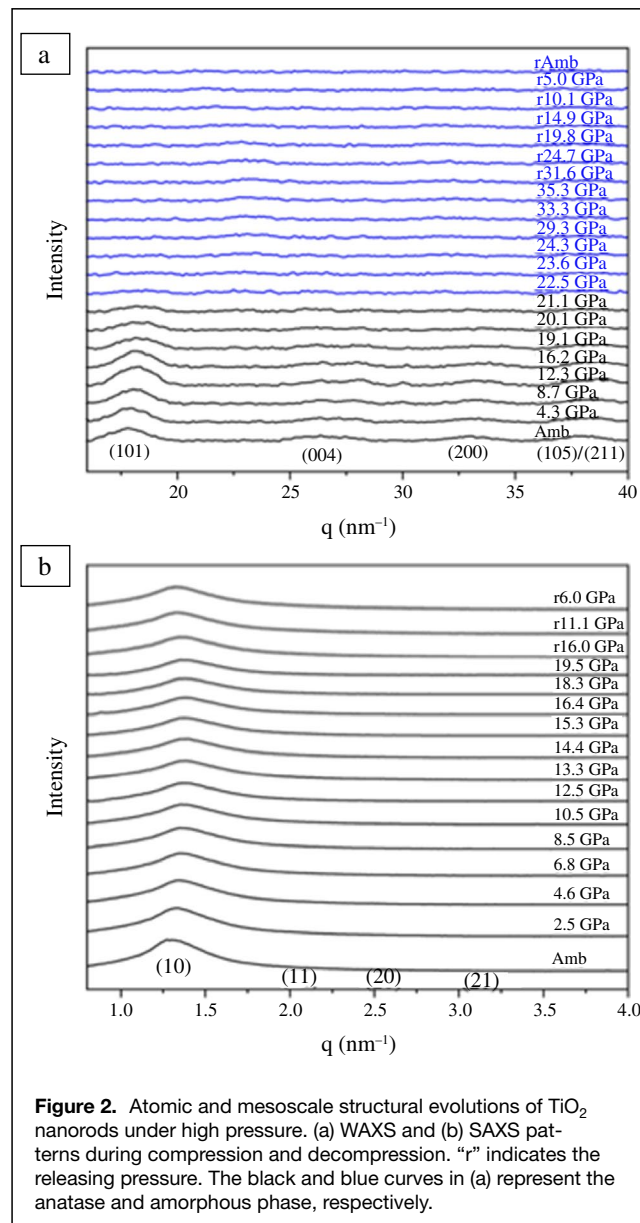
Next, the DACs were compressed with controlled increase in hydrostatic pressures, and *in situ* synchrotron SAXS/WAXS measurements were performed at each stabilized pressure point. **Figure 2a** shows the WAXS profiles collected on a TiO₂ nanorod sample. The initial tetragonal anatase structure remains stable up to ~ 21.1 GPa. At about 22.5 GPa, all the WAXS signals corresponding to the initial anatase structure start to disappear with no new emerging signals, which suggest amorphization of the TiO₂ NCs. These NCs then remained amorphous up to 35 GPa, before it was gradually released back to ambient pressure, where the amorphous nature remains. Such pressure-induced amorphization has been previously reported to occur in TiO₂ anatase nanospheres below 10 nm,⁶ in TiO₂ nanotubes,^{11,12} and in 1D TiO₂-B nanoribbons.⁸ Our observation represents the first example of high pressure-induced amorphization observed in solid 1D TiO₂ anatase NCs. Previous high pressure studies of solid anatase TiO₂ nanowires showed that the phase transition sequence of nanowires with a diameter of 50–200 nm is similar to that in spherical NCs with size larger than 10 nm.^{9,10} The observed differences in our study also demonstrate that the phase transition pathway of solid 1D TiO₂ nanostructures is sensitive to both NC sizes and shapes. **Figure S4a** (SI) shows the pressure-dependent changes in the normalized unit cell parameters (a/a_0 , c/c_0) for TiO₂ nanorods, where the *c*-axis is found to be more compressible than the *a*-axis. Such anisotropic behavior in the compressibility between the *a*-axis and *c*-axis is a structural characteristic of the anatase TiO₂ NCs, which is generally attributed to the differences in terms of the directional population of the TiO₆ and O₆ octahedra sites between the *a*-axis and *c*-axis, and it's in agreement with the quantum-mechanical simulation studies.²⁷ The change of unit cell volume as a function of pressure is shown in **Figure S5a** (SI). By fitting the pressure–volume data to a second-order Birch–Murnaghan equation of state, the bulk modulus (B_0) of anatase TiO₂ nanorods was determined to be 209.24 ± 4.09 GPa, larger than that of the bulk TiO₂ (180 GPa)²⁸ and long nanorods (176 GPa).⁹ Molecular dynamics methods have



been previously used to simulate compression mechanism of TiO₂ NCs, which suggests that such observed ultrastability and enhanced stiffness of nano-anatase are related to the nucleation and growth criteria.²⁹

At the mesoscale, the pressure is controlled below 20 GPa as the coalescence or sintering process often occurs at ~ 10 GPa when silicon oil starts to solidify, and a uniaxial compression is applied on the sample.² SAXS patterns shown in Figure 2b indicate that upon compression up to 20 GPa, the SAXS peaks corresponding to 2D hexagonal mesophase shifted to a higher scattering angle (lower d -spacing) as a result of shrinkage of interparticle distances. Such behavior can be more clearly observed by plotting the change in d -spacing of the first small-angle diffraction peak as a function of pressure (Figure S6a, SI). When the pressure was released from 20 GPa, all SAXS peaks returned to lower angles similar to those before compression, indicating the lack of overall structural changes at the mesoscale.

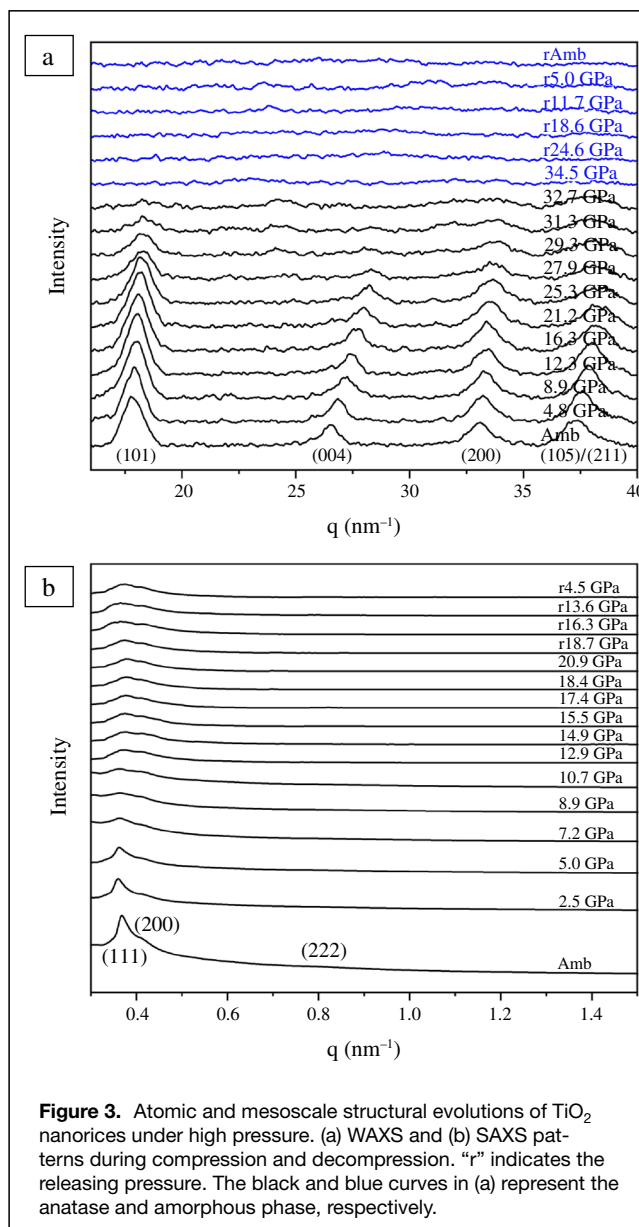
Similarly, the atomic and mesoscale structural evolutions of TiO₂ nanorices are shown in Figure 3. *In situ* high pressure WAXS patterns (Figure 3a) show that with increasing pressure, WAXS peaks display a noticeable red-shift, indicating a pressure-induced reduction of d -spacing and a shrinkage of the atomic unit cell volume. At 31.3 GPa, NCs began to transform from anatase to an amorphous phase, as indicated by the broadening and decreases in all peaks. At 34.5 GPa, WAXS pattern displays a significantly weakened intensity,



indicative of a complete high pressure-induced amorphization. The amorphization pressure in nanorices is similar to TiO₂ nanotubes with outer diameters of 8–10 nm,¹¹ but higher than that of the nanoribbons⁸ and nanotubes with larger diameters (100 nm),¹² and also higher than the solid nanorods in the current study. This is understood from the smaller sizes of TiO₂ nanorices. Pressure dependent changes of lattice parameters (a/a_0 , c/c_0) for TiO₂ nanorices and the evolution of unit cell volumes are shown in Figures S4b and S5b (SI), respectively. The bulk modulus of anatase nanorices was determined to be 198.43 ± 2.32 GPa, larger than that of the bulk material.²⁸ Our results suggest that rice-shaped anatase TiO₂ NCs exhibit lower bulk modulus comparing to the rod-shaped TiO₂ NCs, in contrary to previous work by Park et al.⁷ Possible causes could

be the differences in synthesis and pressure transmitting media used. In addition, the as-synthesized nanorices have a tetragonal bipyramidal shape,²⁵ instead of the cylindrical shapes as in nanorods, which could also influence the lattice compressibility. *In situ* SAXS patterns (Figure 3b) indicate that, upon continuous increase of pressure to 20 GPa, the observed fcc peaks shift to higher angle (lower *d*-spacing) due to the compression of nanoparticle arrays (Figure S6b, SI). Upon release of pressure, the fcc peaks reverted back to smaller angles, and no mesoscale structural transition was observed.

We further carried out TEM analysis on samples after compression up to 20 GPa from the SAXS experiments. Intriguingly, even though SAXS analysis showed no superlattice transformation at the mesoscale associated with pressure changes, pressure-induced morphological transition was observed by TEM for both samples. For TiO₂ nanorods, three different morphologies were found coexisting in the recovered sample: (1) nano-squares or nano-rectangles with an average long edge length of 11.5 ± 2.2 nm (Figures 4a, S7a, SI); (2) large aggregates of broken nanorods (Figure S7b, SI); and (3) nanorods with unchanged shape and width (2.8 ± 0.5 nm), but with shorter length of 12.2 ± 3.0 nm (Figure S7c, SI). The lattice spacing of recovered TiO₂ nanostructures were measured to be 3.5 Å (Figure 4b and insets in Figure S7a, c, SI), which corresponds to (101) planes of anatase TiO₂. This result is consistent with WAXS data sets as the high pressure-induced amorphization did not occur below 20 GPa. We hypothesize that when the nanorod arrays were compressed at pressure greater than 9 GPa, silicon oil can no longer provide a hydrostatic compression environment.³⁰ We speculate that an anisotropic pressure gradient along the compression direction destabilized the ordering of NCs and initiated the detachment of organic ligands. Under high pressure compression, organic ligands may be removed from the nanorod surface, leading to an increase in surface tension. In addition, nanorods can be easily broken under high pressure because of their large aspect ratio. As a result, the NCs came into contact and subsequently fuse into irregular shaped nanostructures (nano-squares or nano-rectangles) to minimize surface area and reduce surface energy, similar to the mechanisms previously reported for PbS nanospheres²² and perovskite nanocubes.²³ In case of TiO₂ nanorices, connected tetragonal bipyramidal nanowires were obtained after compression (Figure 4c). The width of the nanowire was measured to be 4.4 ± 1.1 nm, consistent with the widths of nanorices before compression, with length up to 60 nm (Figure S8a, SI). The nanowires also show *d*-spacing of ca. 3.5 Å, corresponding again to the (101) planes of anatase TiO₂. Such high pressure-induced sintering of NCs into nanowires and nanorods has been previously demonstrated for various particles, and if this morphology transition is universal, the corresponding SAXS pattern would show a blue-shift with increasing pressure that indicates a mesoscale structural transition.² However, the focus in previous studies was mostly set on isotropic



nanospheres, our results provide an example in which high pressure can induce the sintering process of anisotropic NCs, the outcomes of which depend on the shape and size of NCs, and are not straightforwardly predictable. Since we still observed large numbers of NCs with their original shapes after compression (Figures S7c and S8a, SI), the lack of mesoscale phase transition characterized by SAXS can be explained.

Conclusion

In summary, we report the high pressure phase transition behaviors of self-assembled TiO₂ arrays. 1D TiO₂ nanorods and nanorices were synthesized and self-assembled into

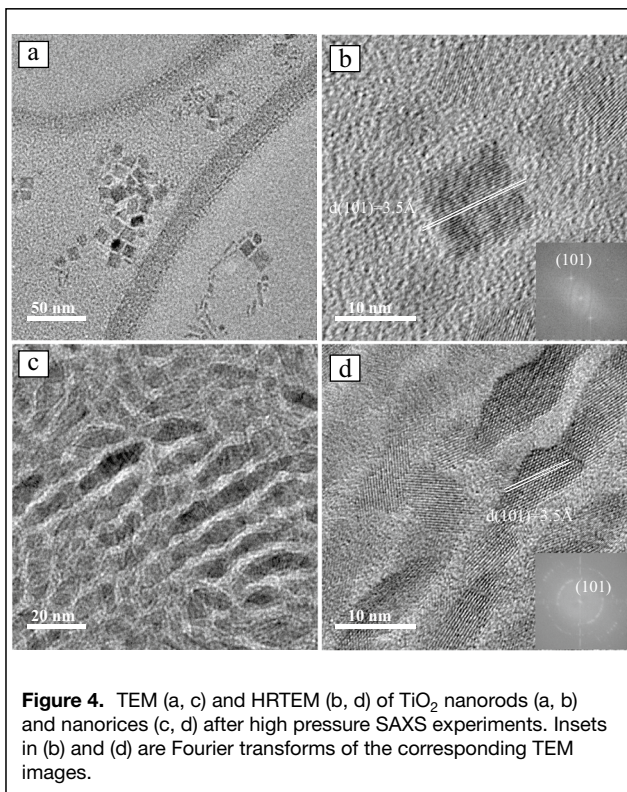


Figure 4. TEM (a, c) and HRTEM (b, d) of TiO₂ nanorods (a, b) and nanorices (c, d) after high pressure SAXS experiments. Insets in (b) and (d) are Fourier transforms of the corresponding TEM images.

ordered hexagonal and fcc mesophase, respectively. Pressure-induced amorphization was observed by *in situ* synchrotron WAXS for both samples, at different onset pressures. Although SAXS data did not reveal a mesoscale structural phase transition of the NC arrays, TEM analysis demonstrated significant changes in the morphology after compression. Under non-hydrostatic pressure, anisotropic compression of TiO₂ NC arrays led to the sintering of nanorods into nano-squares or nano-rectangles, nanorices into nanowires through a deviatoric stress-induced interparticle coalescence. The observed pressure-induced morphological changes will contribute to the rational design of multifunctional materials by pressure-driven fabrication.

Materials and methods

Synthesis of TiO₂ nanorods and nanorices were carried out following previous reported methodologies (see details in the SI).^{24,25} After purification, NCs were dissolved in toluene, dropped onto carbon-coated TEM grids (Ted Pella), and allowed to dry. High resolution TEM (HRTEM)/TEM imaging was performed using a JEOL 2010 F microscope operating at 200 kV at The University of New Mexico.

The NC array is formed by dissolving 80 mg TiO₂ NCs and 20 mg polystyrene (molecular weight 1.7 k) in toluene and then drop-casting ~0.5 mL of the toluene colloidal solution (100 mg/mL) on a Si wafer surface and allowing the organic solvent to evaporate inside a fume hood. *In situ* high pressure experiments were performed by loading a small piece of the

as-prepared NC film along with a few ruby pieces as a pressure marker in a symmetric diamond anvil cell (DAC) with flat culets of 300 μm . A pre-indented rhenium gasket with a hole diameter of 170 μm upon drilling was used as the sample chamber. Silicon oil was used as the pressure transmitting medium. The pressure was determined by measuring the shift in the R1 fluorescence line of ruby. Synchrotron SAXS and WAXS measurements were carried out at the 16-ID-D beamline ($\lambda=0.6199$ Å) and 16-BM-D ($\lambda=0.41328$ Å) at Advanced Photon Source (APS), Argonne National Laboratory (ANL), respectively. A MAR 345 Image Plate Detector was used for recording the diffraction pattern (~3100 mm sample-to-detector distance for SAXS measurements; ~290 mm sample-to-detector distance for WAXS measurements). The 2D diffraction images were transformed into 1D patterns using the DIOPTAS software.

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Conflict of interest

On behalf of all authors, the corresponding authors state that there is no conflict of interest.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1557/s43577-021-00250-w>.

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