Video Article

Synthesis and Exfoliation of Discotic Zirconium Phosphates to Obtain Colloidal Liquid Crystals

Yi-Hsien Yu[1], Xuezhen Wang[2,3], Abhijeet Shinde[2], Zhengdong Cheng[1,2,3,4]

[1]Department of Materials Science and Engineering, Texas A&M University

[2]Artie McFerrin Department of Chemical Engineering, Texas A&M University

[3]Mary Kay O'Connor Process Safety Center, Texas A&M University

[4]Professional Program in Biotechnology, Texas A&M University

Correspondence to: Zhengdong Cheng at zcheng@mail.che.tamu.edu

URL: http://www.jove.com/video/53511
DOI: doi:10.3791/53511

Keywords: Chemistry, Issue 111, zirconium phosphate, synthesis, hydrothermal, microwave-assisted, reflux, dispersity, exfoliation, discotic liquid crystal

Date Published: 5/25/2016

Citation: Yu, Y.H., Wang, X., Shinde, A., Cheng, Z. Synthesis and Exfoliation of Discotic Zirconium Phosphates to Obtain Colloidal Liquid Crystals. *J. Vis. Exp.* (111), e53511, doi:10.3791/53511 (2016).

Abstract

Due to their abundance in natural clay and potential applications in advanced materials, discotic nanoparticles are of interest to scientists and engineers. Growth of such anisotropic nanocrystals through a simple chemical method is a challenging task. In this study, we fabricate discotic nanodisks of zirconium phosphate [$Zr(HPO_4)_2 \cdot H_2O$] as a model material using hydrothermal, reflux and microwave-assisted methods. Growth of crystals is controlled by duration time, temperature, and concentration of reacting species. The novelty of the adopted methods is that discotic crystals of size ranging from hundred nanometers to few micrometers can be obtained while keeping the polydispersity well within control. The layered discotic crystals are converted to monolayers by exfoliation with tetra-(n)-butyl ammonium hydroxide [$(C_4H_9)_4NOH$, TBAOH]. Exfoliated disks show isotropic and nematic liquid crystal phases. Size and polydispersity of disk suspensions is highly important in deciding their phase behavior.

Video Link

The video component of this article can be found at http://www.jove.com/video/53511/

Introduction

Discotic colloids are naturally abundant in the form of clay, asphaltene, red blood cells, and nacre. A range of applications in many engineered systems, including polymer nanocomposites[1], biomimetic materials, functional membranes[2], discotic liquid crystal studies[3] and Pickering emulsion stabilizers[4] are developed based on discotic colloidal nanodisks. Nanodisks with uniformity and low polydispersity is important for studying phases and transformations of liquid crystals. Zirconium phosphate (ZrP) is a synthetic nanodisks with well-ordered layered structure and controllable aspect ratio (thickness over diameter). Therefore, the exploration of different synthesis of ZrP helps to establish fundamental understanding of discotic liquid crystal system.

The structure of ZrP was elucidated by Clearfield and Stynes in 1964[5]. For the synthesis of layered crystals of ZrP, hydrothermal and reflux methods are commonly adopted[6,7]. Hydrothermal method gives a good control on size ranging from 400 to 1,500 nm and polydispersity within 25%[6], while reflux method gives smaller crystals for the same duration time. Microwave heating has been proven to be a promising method for synthesis of nanomaterials[8]. However, there are no papers describing synthesis of ZrP based on microwave-assisted route. The effective control over size, aspect ratio, and mechanism of the crystal growth by hydrothermal method was systematically studied by our group[6].

ZrP can be easily exfoliated into monolayers in aqueous suspensions, and the exfoliated ZrP have been well established as liquid crystal materials in Cheng's group[3,9-13]. So far, exfoliated ZrP nanodisks with various diameters, say different aspect ratios, have been studied to conclude that larger ZrP had the I (isotropic)-N (nematic) transition at lower concentration compared to smaller ZrP[3]. The polydispersity[3], salt[9] and temperature[10,11] effects on the formation of nematic liquid crystal phase have been also considered. Moreover, other phases, such as sematic liquid crystal phase, have been investigated as well[13,14].

In this article, we demonstrate experimental realization of such a colloidal ZrP nanodisks suspension. Layered ZrP crystals are synthesized via different methods, and then are exfoliated in aqueous media to obtain monolayer nanodisks. At the end, we show liquid crystal phase transitions exhibited by this system. A notable aspect of these disks is their highly anisotropic nature that the thickness to diameter ratio is in the range of 0.0007 to 0.05 depending on the size of disks[3]. The highly anisotropic monolayer nanodisks establish a model system to study phase transitions in the suspensions of nanodisks.

Protocol

1. Synthesis of α-ZrP Using Hydrothermal Method

1. Dissolve 6 g of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in 3.75 ml deionized (DI) water in a 150 ml round bottom flask.
2. Add 48 ml of 15 M phosphoric acid (H_3PO_4) dropwise to the $ZrOCl_2$ solution prepared in step 1.1 followed by adding 8.25 ml deionized (DI) water under vigorous stirring.
3. Pour resulting gel-like mixture into Teflon-lined pressure vessel of 80 ml volume. Place the vessel into hydrothermal autoclave composed of stainless steel shell and lid, pressure plate and then tighten well.
4. Place the hydrothermal autoclave into convection oven at 200 °C for 24 hr.
5. After the reaction, allow the hydrothermal autoclave to cool down 8 hr to room temperature under ambient cooling.
6. Collect α-ZrP disks in centrifuge tube after cooling using centrifuge at 2,500 x g for 10 min. Collect liquid portion in waste disposal container since the supernatant liquid contains unreacted phosphoric acid which is corrosive.
    1. Afterwards, add 40 ml of water to α-ZrP, vortex for 1 min and centrifuge at 2,500 x g for 10 min again. Repeat this step 3 times to ensure that all of the acid is washed away.
7. Dry ZrP-water sticky mixture in oven at 65 °C for 8 hr and then grind it using a pestle and mortar.

2. Synthesis of α-ZrP by Reflux Method

1. Mix 6 g of $ZrOCl_2 \cdot 8H_2O$ with 50 ml of 12 M phosphate acid in a 150 ml round bottom flask.
2. The mixture prepared in step 2.1 is reflux in oil bath at 94 °C for 24 hr.
3. Wash the product with DI water three times following same protocol in step 1.6, and then dried in the oven at 65 °C for 8 hr.
4. Grind dried bulky sample into powder using a pestle and mortar, and stock for later use.

3. Synthesis of α-ZrP by Microwave-assisted Method

1. Add 1 g of $ZrOCl_2 \cdot 8H_2O$ into 9 ml of 12 M phosphoric acid solution, and stir the resulting mixture well in a 20 ml scintillation vial.
2. Pour 5 ml of the above mixture into a 10 ml glass vessel specified for microwave reactor.
3. Set reaction temperature at 150 °C, pressure limit at 300 psi and allow the reaction to happen for 1 hr.
4. After the reaction, let the glass vessel cool down for about 15 min and then follow the same procedure as in Steps 1.6-1.7 for acid washing and drying of α-ZrP crystals.

4. Exfoliation of Layered α-ZrP into Monolayers

1. Disperse 1 g of α-ZrP into 10 ml of DI water in a 20 ml scintillation vial.
2. Add 2.2 ml of TBAOH (40 wt. %) to it and vortex for at least 40 sec. Notice that molar ratio of Zr:TBAOH is kept as 1:1.
3. Sonicate the resulting concentrated suspension for 1-2 hr and leave for 3 days to allow full intercalation of TBA^+ ions and complete exfoliation of crystals. Optionally, concentrated suspension can be diluted (2 to 3 times dilution) with water to obtain better exfoliation.
4. Centrifuge the exfoliated samples at high rotation speed (2,500 x g) for 1 hr to remove partially exfoliated crystals settled at the bottom. Collect the top part (exfoliated ZrP) in another container, and repeat the procedure until no sediment is found.

Representative Results

Figure 1a-c show SEM images of α-ZrP nanodisks obtained from hydrothermal, reflux, and microwave-assisted methods, respectively. It was observed that α-ZrP nanodisks show hexagonal in shape and different thickness depending on synthesis conditions and prepared methods. A previously reported study from our group[6] suggests that for the crystal growth time 48 hours or above, the edge of the disks become sharper. Usually, the reflux method yields nanodisks smaller in size and less regularly hexagonal in shape than the α-ZrP obtained by hydrothermal method at similar reaction conditions including concentration of phosphoric acid and reaction time[6,7]. **Figure 1d** shows DSL result of the size distribution of exfoliated ZrP suspensions by three different synthesize methods accordingly.

Figure 2 shows the TEM images of α-ZrP crystals made by microwave-assisted method. It was observed in **Figure 2a** that some crystals were formed after 10 min of microwave dielectric heating. Although some well-defined hexagonal shapes of α-ZrP could be found, most of the obtained crystals are neither regular in shape nor uniform in size. When reaction time was increased from 10 min to 60 min, a sharp and regular hexagonal shape of α-ZrP crystal was formed, indicating better crystallinity of the final products. In this study, required reaction time for synthesis of α-ZrP is significantly reduced with assistance of microwave dielectric heating from days to less than an hour. Therefore, a quick evaluation of parameters and design for fabrication of nanomaterials could be achieved by microwave-assisted method.

Figure 3a shows a schematic illustration of the exfoliation process of multilayer crystal into monolayers. The physical appearance of exfoliated suspension is pearly white (**Figure 3b**) while that of unexfoliated suspension is turbid white. In order to check stability of the dispersion of ZrP nanodisks, the dispersion solution was centrifuged for an hour at high (4,000 rpm, 2,500 x g) rotation speed. However, no sedimentation was observed which proved that dispersions in water are stable due to repulsion force of surface charges on ZrP nanodisks. The exfoliated samples after centrifugation sometimes give very small amount of sediment on account of partially exfoliated ZrP. Top part is considered as well-exfoliated.

Figure 4 shows samples with increasing concentration of ZrP monolayers from left to right as observed between pair of crossed polarizers. As the concentration is increased, nematic fraction is increased as well.

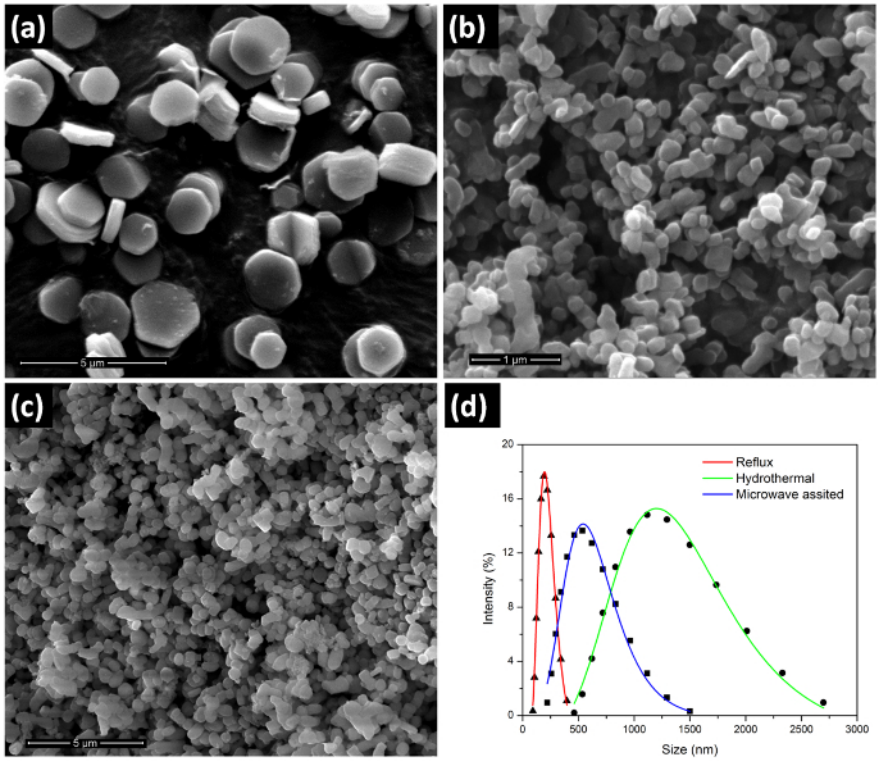

Figure 1. The SEM images of pristine α-ZrP prepared from zirconyl chloride octahydrate via (**a**) hydrothermal reaction in 12 M H_3PO_4 at 200 °C for 24 hr; (**b**) reflux method in 3 M H_3PO_4 at 95 °C for 24 hr; (**c**) microwave-assisted method in 15 M H_3PO_4 for at 200 °C for 1 hr; (**d**) DLS nanodisks size analysis for exfoliated ZrP suspensions prepared by hydrothermal, reflux, and microwave-assisted methods. Please click here to view a larger version of this figure.

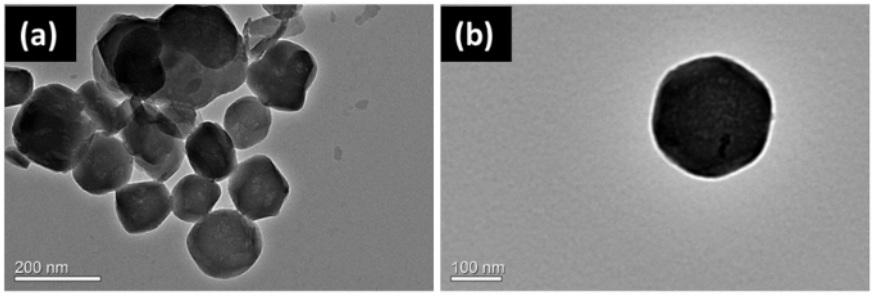

Figure 2. TEM images of the microwave-assisted growth of α-ZrP crystals at 150 °C for (**a**) 10 min and (**b**) 60 min. Please click here to view a larger version of this figure.

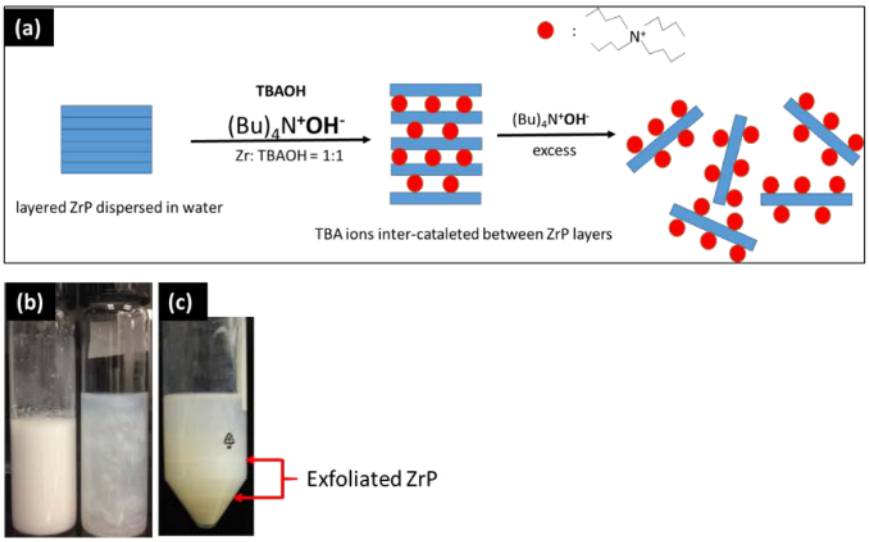

Figure 3. (**a**) Schematic of process of exfoliation of layered zirconium phosphate using tetra (n) butyl ammonium hydroxide, TBA^+ ions, cover ZrP disk on either sides. Overall charge in the system is zero as oxygen on surface of disks carries a negative charge. At ZrP:TBAOH molar ratio 1:1, almost all TBA^+ ions are on the surface of ZrP. As the amount of TBA^+ ions are increased, TBA^+ ions surround ZrP disks from both sides. Inset shows the electrostatic interaction between oxygen (part of ZrP) and TBA^+ ions on the surface of nanodisks. (**b**) Unexfoliated (left) and exfoliated (right) α-ZrP suspensions. (**c**) Exfoliation and fractionation of α-ZrP prepared from reflux method and only exfoliated ZrP in the middle layer is collected (as marked). Please click here to view a larger version of this figure.

Figure 4. ZrP nanodisks suspensions with increasing concentrations from left to right observed between crossed polarizers. Volume fraction of the nanodisks from left to right: 0.38%, 0.44%, 0.50%, 0.53%, 0.56%, 0.63%, 0.75% and 1% respectively. The colorful portions indicate nematic ordering of disks. Due to gravity, nematic tactoids settle at the bottom. This picture is taken after 3 days of gravity sedimentation of nematic tactoids.

Discussion

The reflux method is a good option for making a smaller size of α-ZrP with a uniform diameter and thickness. Similar to the hydrothermal method, the reflux method is limited by the preparation time. In general, it takes longer time for the crystals to grow.

The longer reaction time required for reflux method may result in nanodisks with a larger size. The average size of exfoliated nanodisks is measured by dynamic light scattering (DLS). In this study, the size of exfoliated ZrP nanodisks is 1021.5 nm with 19.6% polydispersity, 289.8 nm with 7.0% polydispersity, and 477.5 nm with 19.1% polydispersity for hydrothermal method (12 M H_3PO_4, 24 hr), reflux method (12 M H_3PO_4, 24 hr) and microwave-assisted synthesis (15 M H_3PO_4, 1 hr) respectively. We also have found that the reflux method can be used to synthesize a different phase of ZrP, theta-ZrP (θ-ZrP) which has larger interlayer spacing compared to α-ZrP, by changing the mixture procedure and the concentration of the materials. For example, θ-ZrP disks with a mean size of 120 nm and thickness of 12 nm were prepared via the reflux method starting with drop-wise addition of 35 wt% H_3PO_4 into a diluted solution of $ZrOCl_2$[15]. In order to obtain uniform α-ZrP nanodisks,

the most critical step in the synthesis procedure is to ensure that all of the precursors are well mixed. When phosphoric acid is introduced into $ZrOCl_2$ solution, the gel will be quickly formed without stirring. The existence of the gel will result in non-uniform nanodisks or nanodisks with low crystallinity.

The microwave-assisted method is an emerging technique for nanomaterial synthesis. In a general microwave-assisted synthesis of ZrP procedure, water serves as a medium microwave absorber[8], which is able to efficiently convert microwave energy into heat. When water molecules are being irradiated by microwave, the dipoles in water molecules tend to align themselves with the applied electromagnetic field accordingly. As a result, energy from dielectric heating and friction between water molecules is released as heat. Thus, heat is generated internally, and is more efficient than external heat transfer that takes place in conventional oven. In microwave-assisted method, a relatively low reaction temperature (150 °C) and shorter reaction time (10 min and 60 min) are found to result in desired size of α-ZrP.

Liquid-crystalline phases of exfoliated ZrP nanodisks are interesting because of highly anisotropic (thickness to size ratio is very small) nature and electrostatic interactions between nanodisks. Isotropic to nematic transition is observed at very low volume fractions of ZrP because of high anisotropy. Nematic tactoids nucleate, grow and settle due to gravity. As a result, nematic phase is formed at the bottom as can be seen in **Figure 4**. The long time effect of gravity causes compression of crystals which is currently being studied in our lab. Due to charges on the surface, the electrostatic interactions between nanodisks play an important role in determining the self-assembly of nanodisks. The complete phase diagram of naturally abundant nanodisks is yet to be fully understood. Besides the formation of the liquid crystalline phases[11], ZrP has potential applications in drug delivery[15]. Monolayer ZrP is a good candidate as the nanodisks for nanocomposites, such as thin film[16].

Disclosures

There is nothing to disclose.

Acknowledgements

This work is partially supported by NSF (DMR-1006870) and NASA (NASA-NNX13AQ60G). X. Z. Wang acknowledges support from the Mary Kay O'Connor Process Safety Center (MKOPSC) at Texas A&M University. We also thank Min Shuai for her guidance.

References

1. Usuki, A., Hasegawa, N., & Kato, M. Polymer-clay nanocomposites. *Adv. Polym.* **179**, 135-195 (2005).
2. Varoon, K. *et al.* Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane. *Science.* **334**, 72-75 (2011).
3. Mejia, A. F. *et al.* Aspect ratio and polydispersity dependence of isotropic-nematic transition in discotic suspensions. *Phys. Rev. E.* **85**, 061708 (2012).
4. Bon, S. A. F., & Colver, P. J. Pickering miniemulsion polymerization using Laponite clay as a stabilizer. *Langmuir.* **23**, 8316-8322 (2007).
5. Clearfield, A., & Stynes J. A. The preparation of crystalline zirconium phosphate and some observations on its ion exchange behaviour. *J. Inorg. Nucl. Chem.* **26,** 117-129 (1964).
6. Shuai, M., Mejia, A. F., Chang, Y. W., & Cheng, Z. Hydrothermal synthesis of layered alpha-zirconium phosphate disks: control of aspect ratio and polydispersity for nano-architecture. *Crystengcomm.* **15**, 1970-1977 (2013).
7. Sun, L., Boo, W. J., Sue, H.-J., & Clearfield, A. Preparation of α-zirconium phosphate nanoplatelets with wide variations in aspect ratios. *New J. Chem.* **31**, 39-43 (2007).
8. Gawande, M. B., Shelke, S. N., Zboril, R., & Varma, R. S. Microwave-sssisted chemistry: synthetic applications for rapid assembly of nanomaterials and organics. *Accounts Chem. Res.* **47**, 1338-1348 (2014).
9. Chang, Y.-W., Mejia, A. F., Cheng, Z., Di, X., & McKenna, G. B. Gelation via Ion Exchange in Discotic Suspensions. *Phys. Rev. Lett.* **108**, 247802 (2012).
10. Wang, X. *et al.* Thermo-sensitive discotic colloidal liquid crystals. *Soft Matter.* **10**, 7692-7695 (2014).
11. Li, H., Wang, X., Chen, Y., & Cheng, Z. Temperature-dependent isotropic-to-nematic transition of charged nanoplates. *Phys. Rev. E.* **90,** 020504 (2014).
12. Chen, M., *et al.*, Observation of isotropic–isotropic demixing in colloidal platelet–sphere mixtures. *Soft Matter.* **11** (28), 5775-5779 (2015).
13. Sun, D., Sue, H.-J, Cheng, Z., Martinez-Raton, Y., & Velasco E. Stable smectic phase in suspensions of polydisperse colloidal platelets with identical thickness. *Phys. Rev. E.* **80**, 041704(1-6) (2009).
14. Wong, M. *et al.* Large-scale self-assembled zirconium phosphate smectic layers via a simple spray-coating process. *Nat. Commun.* **5**, 3589 (2014).
15. Diaz, A. *et al.* Zirconium phosphate nano-platelets: a novel platform for drug delivery in cancer therapy. *Chem. Commun.* **48**, 1754-1756 (2012).
16. Kim, H.-N., Keller, S. W., Mallouk, T. E., Schmitt, J., & Decher, G. Characterization of zirconium phosphate/polycation thin films grown by sequential adsorption reactions. *Chem. Mater.* **9**, 1414-1421 (1997).

