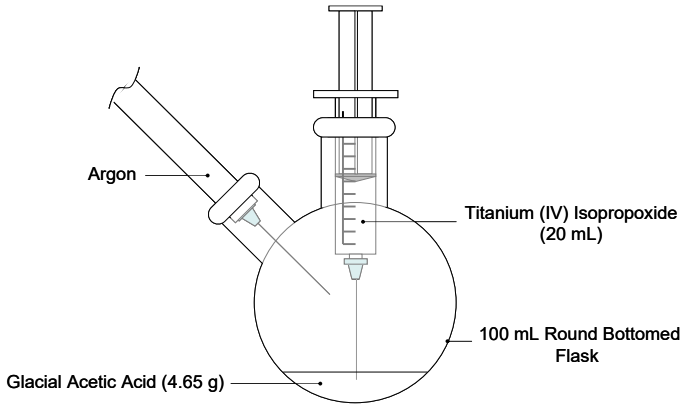
Sol-Gel TiO_2 Prep – Standard Operating Procedure

NOTE: Before reading this you MUST read the 'SOP - Energy and environmental impacts under normal, abnormal and emergency conditions' which is Mills group web site, https://www.profandrewmills.com/leaf-documents/. This addresses general energy and environmental impacts under normal, abnormal and emergency conditions considerations which you NEED to be cognisant of before conducting any experiment. If you identify anything in an SOP which can be improved, please contact the LO and PI to discuss the proposed change(s) before putting them into effect.

1. Add 20 mL of titanium (IV) isopropoxide ($Ti(OPr^i)_4$) is added to a 100 mL round bottomed flask containing 4.65 g of glacial acetic acid using a syringe.

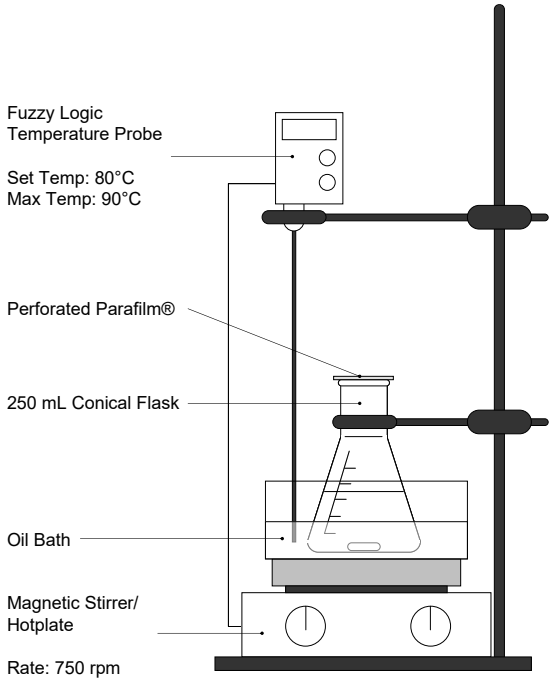


   As $Ti(OPr^i)_4$ is extremely moisture sensitive, the tip of the needle should be kept below the surface of the acetic acid when adding. As an extra precaution, argon can be flushed through the round bottomed flask, but is usually unnecessary. Upon addition, the reaction of the $Ti(OPr^i)_4$ with the acetic acid is noticeably exothermic.

2. After ca. 1 min, the resulting $Ti(OPr^i)_4$ solution should then be transferred to a 250 mL conical flask containing 120 mL of distilled water and 1.08 g of concentrated nitric acid. A clear gel will form.

3. Place a magnetic stirrer bar into to the flask before covering the top with Parafilm®. Pierce a few holes in Parafilm® with a syringe needle.

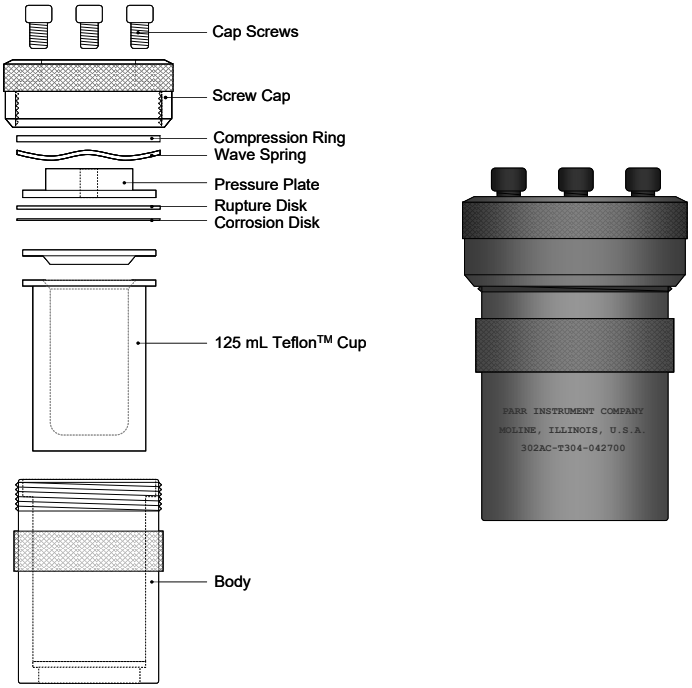
4. Secure the flask in a paraffin oil bath on a stirrer/heating plate as shown and set the Fuzzy Logic temperature controller to maintain a temperature of 80°C.



5. Stir the contents of the flask for 8 h at 80°C.

6. After 8 h, remove the flask from the oil bath and carefully wipe the bottom of the flask clean from any oil. Set the flask aside to cool down overnight.

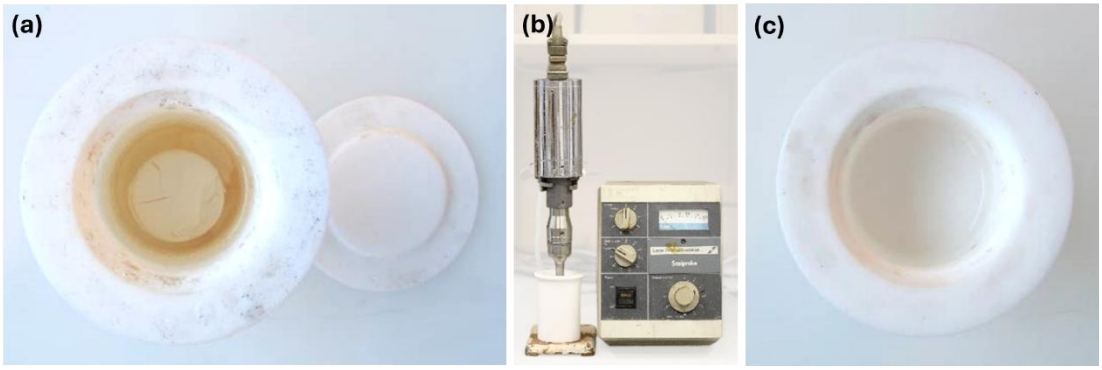
7. The solution should then be filtered through a 0.45 µm syringe filter to remove any non-dispersed aggregates. This solution should be filtered into the 125 mL Teflon™ liner of the Parr Instruments® autoclave. **NOTE**: the maximum volume of liquid in each cup should not exceed 80 mL. There are 2 autoclave setups available, so the filtered solution should be divided equally between both.



8. The autoclave should be assembled as shown above. Ensure the 6 cap screws are securely tightened. If in doubt, ask a colleague to double check.

9. Place the autoclaves inside an oven set at 220°C for 12 h. The high pressure and temperature conditions inside the vessel encourage crystal growth by increasing the solubility of small particles. This then promotes Ostwald ripening to occur.

10. After cooling, the contents will have separated into two phases inside the liner **(a)**, therefore, the solution has to be redispersed using **(b)** an ultra-sonic probe (Soniprobe, Lucas Dawe Ultrasonics) (Duty Cycle = constant, Output control = 3, Timer = 1 min) to obtain a good dispersion **(c)**.



11. Transfer the dispersion into a 250 mL round bottom flask and attach it to the rotary evaporator. The dispersion/paste needs to be concentrated down to 10 – 12 wt%.

12. Set the temperature of the water bath on the rotary evaporator low at first, i.e. 35 – 40°C, and start the rotation before switching on the vacuum pump (Vacuubrand®). The contents should start to slowly bubble. If not, gradually increase the temperature in small increments. The bubbling will steady off and reduce with each increment (2 – 5°C). When the bubbling reduces, that is when the next temperature increase should be made. Typically, the maximum temperature needed is ca. 60°C. If increased too high/quickly, the bubbles can get out of control and the paste/dispersion can get sucked up into the condenser, resulting in a long cleanup.

13. At the point when the solution becomes thick enough to just start to coat the inside of the round bottomed flask, remove the flask from the rotary evaporator.

14. Pre-weigh a small glass vial and then pipette a small amount of the paste into it and weigh it again to determine the initial weight of the paste.

15. Place the vial into a furnace, set at 450°C, for 5 – 10 min in order to evaporate all the liquid.

16. Remove the vial from the furnace carefully using tongs and allow to cool before re-weighing to determine the weight of the remaining solids (TiO_2).

17. Using the initial weight and the dry weight, the wt% should now be determined ((dry weight / initial weight) x 100). If the weight percent is not in the region of 10 – 12 wt%, the flask should be reattached to the rotary evaporator for another few minutes. This process should be repeated until a value of 10 – 12 wt% is attained.

18. When the desired weight percentage of paste has been achieved, scrape the paste out of the round bottom flask into a pre-weighed 30 mL glass jar.

19. The total weight of the paste should then be determined and multiplied by the calculated wt% giving the total weight of solids in the paste.

20. Polyethylene glycol (50 wt% of the total solids) should then be added to the paste as a binder to prevent the formation of small surface cracks when the paste is eventually cast and allowed to dry before annealing.

21. Place a magnetic stirrer bar in the jar of paste and leave stirring overnight. The paste can then be stored in the fridge.