

Synthesis to TiO₂ Colloids Using Acetic Acid (Colloidal Suspension for obtaining transparent mesoscopic TiO₂ films)

Colloid Synthesis

The synthesis of colloids with acetic acid is nearly identical to the synthesis using nitric acid. The main difference is the amount of acid added and the amount of manipulation of the hydrolyzing particle solution necessary. The full synthetic procedure will be described here even though much of this has been repeated elsewhere.

250 ml of millipore H₂O is poured into a 1000 ml round bottom flask. This water can be obtained in Mark Hanna's lab in the SERF. 80 ml of glacial acetic acid is added to the water. The flask is placed in an ice bath and stirred for a few minutes to allow the solution to cool.

10 ml of 2-propanol is added to a dropping funnel followed by 37 ml of Ti(IV)isopropoxide (Aldrich, 99.9%). The degree of purity of the Ti(IV)isopropoxide necessary for making efficient solar cells is not currently clear. Given the expense of the 99.9% grade, experiments with the 97% grade should be undertaken. The dropping funnel is attached to the 1000 ml flask described above and the solution slowly dripped at a rate of approximately one drop per second over the course of 30-40 minutes. The water/acetic acid solution is vigorously stirred during this process (as fast as it would stir without upsetting the stir bar).

This solution should have a very cloudy appearance with large particles of white precipitate floating in it. However, compared to the nitric acid synthesis the solution is much clearer with less precipitate. In this particular instance the Ti(IV)isopropoxide was more yellow than it would have been in a freshly opened bottle. This current synthesis utilized Ti(IV)isopropoxide from a bottle opened 9/20/96 and not used since. The capped bottle was sealed with two strips of parafilm on the outside to prevent water contamination (may or may not be useful to do this, but it makes me feel better, so I do it).

The contents of the 1000 ml flask is poured into a 600 ml flask poured into a 600 ml beaker which is placed in an 80°C oil bath (actually the oil bath was considerably hotter, near 100°C, but the bath cools quite a bit when the beaker is immersed). The solution is heated with vigorous stirring. As the solution heats, the precipitate disappears, the scattered light appears bluish, and the solution becomes viscous. Eventually this solution becomes gel like. At this point I let the solution cool which returns it to a liquid state, then I heat it to 80° again for 3-4 hours. Another purpose to the heating is to reduce overall volume of solution to the 200-250 ml range. This solution is much more viscous than

water and is quite milky, although not nearly as white as milk (sort of a blue color). There should be no visible precipitate at this stage.

Once the heating is finished (3-4 hours, there does not seem to be any real change in particle size with longer heating times, based on optical appearance), the colloidal solution is loaded into the Teflon insert of the titanium autoclave (bomb). One should be careful that the volume of solution is around 200-250 ml. If the volume is larger this, then there is the very remote possibility that the autoclave could rupture if the oven were to overheat (an extremely unlikely event given the safeguards in place, see below), so I fill the autoclave to this conservative limit (see the Parr manual for details on water expansion at elevated temperatures).

After sealing the autoclave I placed it in the oven which was set to a maximum temperature of 230°C (varies depending on desired particle size, larger particles require higher temperatures). The safety relay is engaged and I set the temperature on the safety 10° higher than the oven temperature (so that the whole apparatus does not shutdown due to fluctuations around the setpoint of the oven. N.B. that the safety relay is in Fahrenheit). The oven will also shutdown should the temperature rise more than a few degrees above the setpoint. I set the timer to shut the oven off 13 hours after turning the oven on. This allows one hour for warm up. Generally, I like to run this part of the synthesis overnight when no one is around, another conservative safety step. Also, the oven can be somewhat noisy, so it is better to have it running when people will not be in the lab.

After the cycle is through I let the whole system cool (with the autoclave in the oven) for at least 24 hours. The temperature readout on the safety relay should read room temperature and the autoclave should be at a neutral (ambient) temperature before opening it. Even in this case I use the polycarbonate shield for protection when opening the autoclave. A screwdriver is normally necessary to pry the top off.

The contents of the Teflon insert is emptied into a 400 ml beaker and covered with parafilm. The solution is quite odiferous due to the high concentration of acetic acid. In addition all of the solid component will settle to the bottom of the insert. In order to make the solid component soluble again the solution needs to be sonicated using the cell disrupter in Paul Weaver's lab. A regular sonicator is not powerful enough to break up the particle agglomeration. The main thing to remember is not to touch the tip of the sonic horn to the bottom of the beaker and not to turn on the sonic horn unless the tip is immersed in solution. 5 minutes is plenty of time at a setting of 7-8 or so (using the regular tip, not the micro tip).

After this procedure the solution can sit for many days in the air without separating significantly. Now it is necessary to concentrate the solution to 120-

140g/liter, which I do on the rotary evaporator. This is the most difficult part of the procedure to reproduce. I usually gauge the concentration by assuring 100% yield and measuring the amount of liquid collected (vs. the original volume of solution). Volume markings on the collection flash facilitate this. Note that if one stops pulling water/acetic acid from the solution and lets the rotary evaporator up to air then the solution needs to be cooled. Otherwise the colloidal solution will bump all over the inside of the evaporator. I usually use a bump guard anyway (even though this cannot prevent the bumping after a quick restart without cooling).

Preparation of TiO₂ Films on Conducting Glass Electrodes.

Previously cleaned conducting glass electrodes are laid on a clean surface. Desired amount of TiO₂ suspension is applied through a microsyringe and spread over half the length of the electrode. (We employ 40 mm × 9 mm electrodes cut from conducting glass sheets. These electrodes can be inserted into quartz cuvette for spectroscopic as well as electrochemical measurements.) The electrode is first dried in air and then annealed in air at 673 K. The electrodes can either be stored in a desiccator for future use or further modified with sensitizers by immersing in a dye solution. (Slightly warm electrodes immersed in a dye solution respond well to dye modification)

