Semiconductor Colloids

Colloidal TiO$_2$

Colloidal TiO$_2$ is easily prepared by the hydrolysis of titanium isopropoxide in aqueous or nonaqueous media. The TiO$_2$ colloids are stable in the pH below pH 3 or greater than pH 11. One needs to use a stabilizer (e.g., 1-2% low mol. wt. polyvinyl alcohol) to obtain stable colloidal solution in the pH range of 3-11. It is advisable to prepare 10% titanium isopropoxide solution in isopropanol as a stock solution.

Aqueous solution: Add dropwise solution of titanium isopropoxide slowly to the aqueous solution of 0.1 M HCl or HClO$_4$ with constant stirring. The final concentration of 5-10 M will yield a transparent colloidal suspension. Higher concentration of TiO$_2$ colloidal suspension can be stabilized by decreasing the pH of the medium.


In Acetonitrile: Stir the dry acetonitrile solution in a N$_2$ atmosphere. Inject titanium isopropoxide/isopropanol solution with a 25 microliter syringe several times to attain a concentration of 1-5 mM. This process is extremely sensitive to moisture content in acetonitrile. Stop the addition of titanium isopropoxide once you observe turbidity.


In ethanol: This is by far the best and convenient medium to prepare concentrated (0.01-0.1 M) colloidal TiO$_2$ suspension. Colloidal TiO$_2$ suspension (0.1 M) in ethanol was prepared by the hydrolysis of titanium isopropoxide. The procedure involved dropwise addition of 2.97 mL of titanium isopropoxide solution to an ethanol solution (100mL) kept under vigorous stirring. This stock solution needs to be stored in a closed glass vessel under constant stirring. (If the hydrolysis is carried out in the presence of acetic acid (1-2%) the size of the colloidal particles is relatively small and remains stable even without stirring).

Colloidal SnO₂

Stable suspensions (15%) of SnO₂ can be purchased from Alfa Chemicals

Colloidal WO₃

The suspensions of WO₃ can be prepared in both water and ethanol. Desired amount of sodium tungstate was dissolved in water. Concentrated HCl was added dropwise until the precipitation of tungstic acid was completed. The beaker containing the precipitate is allowed to settle in an icebath. Once the precipitate is settled the supernatant was slowly removed and the precipitate was washed with water. (Decanting the clear solution is better than the filtration method.) Tungstic acid (WO₃.2H₂O) precipitate was the dissolved in water (or ethanol) and the solution is slowly heated on a hotplate. Solid oxalic acid was added at elevated temperatures. The concentration of oxalic acid was varied (0.16-0.31 M) to obtain colloids of different sizes. The diameter of these particles is in the quantum size regime (50 Å) as reflected from the blue-shift in their absorption onset.


Colloidal ZnO

Reflux zinc acetate (100 ml of 0.1 M) in ethanol for 1-2 hours. The solid will dissolve in ethanol at reflux temperature. Attach a drying tube to the outlet to prevent exposure to humidity during cooling. Add ethanol to make up the volume to 100 ml. Store this solution in a desiccator. When required transfer 5 ml of the zinc complex solution into a 50 ml flask and dilute with 20 ml of ethanol. Add LiOH (0.02 M or higher) powder and sonicate the solution for 15 min. in a icebath. The resulting colloidal solution should emit blue light upon exposure to UV light. As the particles grow the emission will shift to green. The particle size can be varied by controlling the hydrolysis temperature. Upon aging for few days the particles grow and emit orange light. 

The emission is totally quenched upon exposing the deaerated suspensions to UV-light, for 30 min. The electron accumulation as evidenced from the shift in the absorption edge, opens up a nonradiative decay pathway for the charge recombination. The emission can be restored upon exposure to air!

