

# Semiconductor Colloids

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## Colloidal TiO<sub>2</sub>

Colloidal TiO<sub>2</sub> is easily prepared by the hydrolysis of titanium isopropoxide in aqueous or nonaqueous media. The TiO<sub>2</sub> 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<sub>4</sub> with constant stirring. The final concentration of 5-10 M will yield a transparent colloidal suspension. Higher concentration of TiO<sub>2</sub> colloidal suspension can be stabilized by decreasing the pH of the medium.

(Bahnmann, D., Henglein, A. and Spanhel, L., Detection of the intermediates of colloidal TiO<sub>2</sub>-catalysed photoreactions. *Faraday Discuss. Chem. Soc.*, 1984, 78, pp 151; *J. Phys. Chem.*, 1984, 88, pp 709-11)

**In Acetonitrile:** Stir the dry acetonitrile solution in a N<sub>2</sub> 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.

Kamat, P. V. and Fox, M. A., Photosensitization of TiO<sub>2</sub> colloids by erythrosin B in acetonitrile. *Chem. Phys. Lett.*, 1983, 102, pp 379-84.

**In ethanol:** This is by far the best and convenient medium to prepare concentrated (0.01- 0.1 M) colloidal TiO<sub>2</sub> suspension. Colloidal TiO<sub>2</sub> 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).

Kamat, P. V., Bedja, I. and Hotchandani, S., Photoinduced charge transfer between carbon and semiconductor clusters. One-electron reduction of C<sub>60</sub> in colloidal TiO<sub>2</sub> Semiconductor suspensions. *J. Phys. Chem.*, 1994, 98, pp 9137-9142

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## Colloidal SnO<sub>2</sub>

*Stable suspensions (15%) of SnO<sub>2</sub> can be purchased from Alfa Chemicals*

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## Colloidal WO<sub>3</sub>

The suspensions of WO<sub>3</sub> 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 (WO<sub>3</sub>·2H<sub>2</sub>O) precipitate was 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.

Nenadovic, M. T., Rajh, T., Micic, O. I. and Nozik, A. J., Electron transfer reactions and flat-band potentials of WO<sub>3</sub> colloids. *J. Phys. Chem.*, 1984, 88, pp 5827-30.

Bedja, I., Hotchandani, S. and Kamat, P. V., Photoelectrochemistry of quantized WO<sub>3</sub> colloids. Electron storage, electrochromic, and photoelectrochromic effects. *J. Phys. Chem.*, 1993, 97, pp 11064-70

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## 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!*

Spanhel, L. and Anderson, M. A., Semiconductor Clusters in the Sol-Gel Process - Quantized Aggregation, Gelation, and Crystal-Growth in Concentrated ZnO Colloids. Journal of the American Chemical Society, 1991, 113, pp 2826-2833

Kamat, P. V. and Patrick, B., Photophysics and photochemistry of quantized ZnO colloids. J. Phys. Chem., 1992, 96, pp 6829-34.

Subramanian, V., Wolf, E. E. and Kamat, P. V., Green Emission to Probe Photoinduced Charging Events in ZnO-Au Nanoparticles. Charge Distribution and Fermi-Level Equilibration. J. Phys. Chem. B, 2003, 107, pp 7479-7485.