

# Core-Shell Particles

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**Caution:** Since the colloid synthesis is sensitive to various laboratory conditions and the practices of the individual researchers, the following procedure should be taken as a general guideline. One may have to vary the experimental conditions to suit their needs.

1. Gold Capped Silica/Alumina Collods
  2. Gold Capped TiO<sub>2</sub> Collods (TiO<sub>2</sub>@Au)
  3. Ag @TiO<sub>2</sub> and Ag@SiO<sub>2</sub> Colloids.
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## Gold Capped Silica/Alumina Collods

Nalco Chemicals markets alumina capped silica colloids that are stable in acidic pH. These colloids are positively charged and electrostatically bind to [AuCl<sub>4</sub>]<sup>-</sup> ions

1. Prepare 10mM HAuCl<sub>4</sub> solution (0.0985g in 25mL of H<sub>2</sub>O).
2. Add 20 mL of the 10 mM HAuCl<sub>4</sub> solution dropwise with vigorous stirring to 20mL solution of 10% SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> solution in water (2mL of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in 20 mL of H<sub>2</sub>O). I used a solution consisting of 3.8 (w/w)% Al<sub>2</sub>O<sub>3</sub> and 19 (w/w)% SiO<sub>2</sub>.
3. Add sodium borohydride solution in water (~10mM) dropwise with vigorous stirring until a color change from pale yellow to dark purple occurs.

See reference, Dawson, A; Kamat, P. V. *J. Phys. Chem. B.* **2000**, *104*,11842-11846

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## Gold Capped TiO<sub>2</sub> Collods (TiO<sub>2</sub>@Au)

5mM TiO<sub>2</sub> Colloids:

1. Prepare 10% titanium(IV) isopropoxide in 1-propanol (or isopropanol):  
  
Dilute 2.5mL of titanium(IV) isopropoxide in 25mL of 1-propanol.
2. Prepare 5mM TiO<sub>2</sub>:

2.97mL of 10% titanium(IV) isopropoxide diluted in 200mL of water. pH of water was adjusted to 1.5 using 1M HClO<sub>4</sub> prior to addition, to stabilize TiO<sub>2</sub> colloids.

**\*\*IMPORTANT:** Add titanium isopropoxide solution slowly, 1 drop at a time, while stirring vigorously, to obtain a clear, colorless solution.

3. Store in a stoppered flask and use freshly prepared.

**Note:** I was able to make TiO<sub>2</sub> colloids of concentrations of up to 15mM. Higher concentrations were less stable and the resulting solutions were whitish and cloudy (not suitable for absorption measurements).

5mM HAuCl<sub>4</sub>:

4. Dissolve 0.1697g of HAuCl<sub>4</sub> in 100mL water.

TiO<sub>2</sub>@Au Colloids:

5. Add desired volume of Au dropwise to TiO<sub>2</sub> colloids while stirring vigorously, to obtain desired concentration.

- I generally worked with [TiO<sub>2</sub>] of 2-4mM and [Au] of 0.06-0.3mM
- **Note:**

For very low [TiO<sub>2</sub>] or very high [Au] (with respect to TiO<sub>2</sub>) then the colloids are unstable.

1. Stir for 5-10 min (to allow all gold to adsorb to TiO<sub>2</sub> surface).

BH<sub>4</sub><sup>-</sup> Reduction:

2. Prepare ~10 mM NaBH<sub>4</sub> in water (use 1mM when TiO<sub>2</sub> concentration is low to avoid aggregation effects):

0.0095g NaBH<sub>4</sub> dissolved in 25mL of water.

3. Add NaBH<sub>4</sub> dropwise to solution with vigorous stirring until a color change to 'wine red' is seen (some gas will be released).

**\*\*IMPORTANT:** Initially a color change to dark purple will be seen. Continue adding NaBH<sub>4</sub> beyond this initial color change until the 'wine red' color is achieved. If the color remains a dark purple despite the addition of more NaBH<sub>4</sub> then the colloids have aggregated. To avoid this, decrease the NaBH<sub>4</sub> concentration and add at a slower rate.

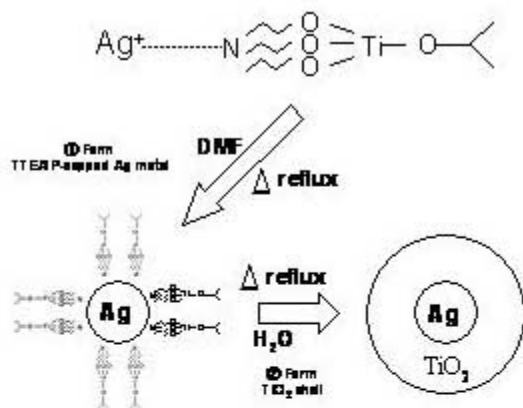
It is also important to note that if the TiO<sub>2</sub> concentration is too low, or the metal concentration is very high then aggregation is likely to occur.

- Continue stirring until gas is no longer forming, then top solution to desired volume using water with pH adjusted to 1.5 (with  $\text{HClO}_4$ ).

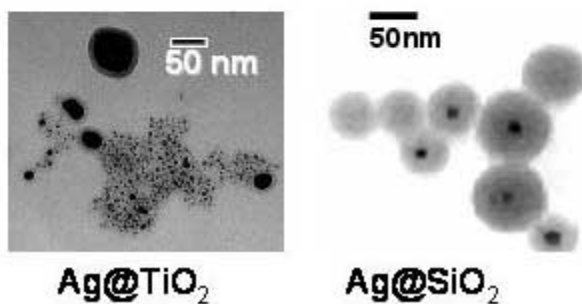
Dawson, A. and Kamat, P. V., Semiconductor-metal nanocomposites. Photoinduced fusion and photocatalysis of gold-capped  $\text{TiO}_2$  ( $\text{TiO}_2/\text{Au}$ ) nanoparticles. *J. Phys. Chem. B*, 2001, 105, pp 960-966.

## Ag @ $\text{TiO}_2$ and Ag@ $\text{SiO}_2$ Colloids.

The synthesis of silver core and  $\text{TiO}_2$  shell requires patience and careful optimization of experimental conditions. If not careful the  $\text{TiO}_2$  clusters are formed separately. The method adopted is as follows



Scheme 2



Desired concentration of TTEAIP (8.3mM, unless otherwise specified) was prepared in iso-propanol. Two mL of 15mM  $\text{AgNO}_3$  solution was mixed with 18mL of TTEAIP solution. Ten mL of DMF was then added into TTEAIP-Ag solution. The concentrations of  $\text{Ag}^+$  and TTEAIP in this solution are 1 mM and 5mM, respectively.

*The volume ratio of DMF and  $i$ -PrOH has been optimized by carrying out several batch preparations. When the amount of DMF was too little or when  $i$ -PrOH was excluded, aggregation of clusters is observed. The volume ratio of DMF and  $i$ -PrOH hence is an important factor in the preparation of the Ag @ $\text{TiO}_2$  clusters.*

The solution was stirred first for 15 minutes at room temperature and then refluxed with continued stirring. With continued heating of the solution, the color slowly changed from colorless to light brown. After 90 min, the color of the suspension turned to

dark brown. At this point the heating was stopped and the suspension was stirred until it cooled down to room temperature. This suspension exhibits a plasmon absorption at 460 nm and shifts to 420 nm upon UV-irradiation in  $\text{N}_2$  purged solutions.

**Silica capped Ag particles** (viz., Ag @ $\text{SiO}_2$ ) were prepared using active silica instead of TTEAIP. The cluster suspension of Ag@ $\text{TiO}_2$  and Ag@ $\text{SiO}_2$  was centrifuged and resuspended in ethanol solution. The procedure was repeated at least 3-times to minimize the content of water and DMF in the suspension.

Hirakawa, T. and Kamat, P. V., Electron Storage and Surface Plasmon Modulation in Ag@TiO<sub>2</sub> Clusters. *Langmuir*, 2004, 20, 5645-5647.

Pastoriza-Santos, I., Koktysh, D. S., Mamedov, A. A., Giersig, M., Kotov, N. A. and Liz-Marzan, L. M., One-pot synthesis of Ag@TiO<sub>2</sub> core-shell nanoparticles and their layer-by-layer assembly. *Langmuir*, 2000, 16, pp 2731-2735.

Ung, T., Liz-Marzan, L. M. and Mulvaney, P., Controlled method for silica coating of silver colloids. Influence of coating on the rate of chemical reactions. *Langmuir*, 1998, 14, pp 3740-3748.