

# Zinc Oxide nano-Colloid solution and fabrication of Transparent conducting Oxide Films

*A project report*

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by

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## **Abstract**

ZnO nanoparticles have shown a great potential to be used for formation of thin transparent conducting oxide films used for various electronic applications mainly because of its high band gap. In this study we prepared ZnO nanoparticles of size ~5nm in colloidal form by different methods, capped with Dodecane thiol( DDT) and Polyvinyl pyrrolidone(PVP). Particles capped With DDT were further washed with various methods to remove precursor impurities present in it and two times ethanol washing was found to give best results. Washed particles dispersed in Chloroform and Toluene are used to fabricate an array over silicone wafer by evaporation guided self assembly method.

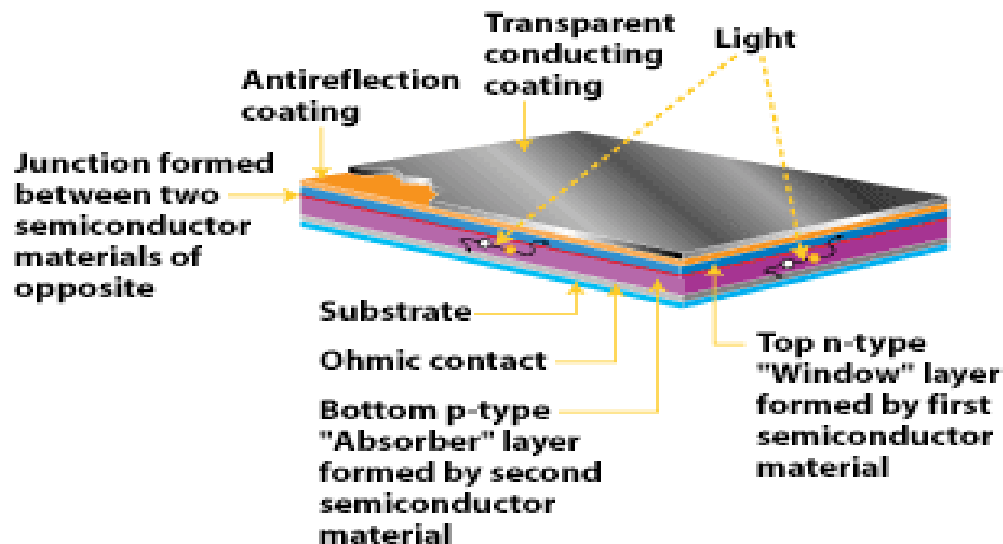
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## **Introduction:**

Transparent conducting films are mainly used as electrodes where they act both as a window for light to pass through to the active material beneath (where carrier generation occurs) and as an ohmic contact for carrier transport out of the photovoltaic. Transparent materials possess band-gap with energies corresponding to wavelengths which are shorter than the visible range (380 nm to 750 nm). As such, photons with energies below the band-gap are not collected by these materials and thus visible light passes through.



1

FIG-1: Application of transparent conducting film in Solar cells

(Source: [http://en.wikipedia.org/wiki/Transparent\\_conducting\\_film](http://en.wikipedia.org/wiki/Transparent_conducting_film))

Over the last decade the applications for transparent conductive films has sky-rocketed. They are used in a host of products that we see all around us and use everyday. Some of these products include display electrodes for today's paper-thin LCD, plasma and organic electroluminescence (EL) televisions as well as touch screen monitors on ATMs, ticket vending machines installed at train stations, car navigation systems, handheld game

consoles, and mobile phones. Transparent conductive films are also used for electrodes in solar cells, which are poised to sweep the market in the near future. Fig 1 show the use of TCO in Solar cells respectively.

Transparent conductive films are essential to electrical products that require thin film materials with superior optical and electrical properties. Besides having excellent transmission characteristics, the resistivity of transparent conductive films must be made as low as possible in order to conserve energy, power and resources. After looking at a number of thin film materials that met all of these requirements, researchers zeroed in on ITO (tin doped indium oxide), which is now the most widely used transparent conductive film material.

Indium is a rare metal and found in very few parts of the world (mainly in China) resulting in very high cost and making it a strategic material. Its clearly visible by the fact that Chinese government has decided [The straits times, June 2, 2010] to impose ban on all the private mining activities in exploration of Indium with some other strategic metals in order to control future price and destination of this metal.

Recently zinc oxide has shown great potential to replace the ITO based transparent conducting oxide films. ZnO has band width of 3.37 eV. This implies that it does not absorb in visible region. Also it is 1000 times more abundant than Indium so replacement will greatly reduce the cost. Recently people[1] have found more than 85% transmittivity and A. Suszuki et al [2] have shown resistivity of  $8.45 \times 10^{-5} \Omega \cdot \text{cm}$  for ZnO thin films. This shows it can be used for various applications mentioned earlier. One of the major beneficiaries of this replacement will be solar cell based technologies because cost is the main obstruction in its large scale applications. For a typical solar cell film thickness around 500nm with sheet resistance of 10ohm/square and visible transmission of 85% is required which can be achieved by ZnO thin films. Swati Sharma et.al. [9] have synthesized ZnO nanoparticles using a simple top-down approach to wet chemistry with stearic stabilization technique. They obtained a highly stable suspension of ZnO nanoparticles. From absorbance measurements, they saw a strong absorbance and a band edge at 376 nm. They have also established a technique for

obtaining a uniform coating of ZnO thin film on a quartz substrate using spin coating followed by a 5-min. annealing at 450°C. I-V measurements were taken show that their ZnO thin film has a conductivity of  $5.303 \times 10^{-7} / \Omega \text{ cm}$ .

In this work we have used wet chemical route to synthesize ZnO nanoparticles. ZnO nano-colloid is used to make 2D array of nanoparticles.

## **Experiment:**

Experiments have been done to prepare ZnO colloidal solution. Issues of precursor impurities present in the colloid thus prepared have been looked into and couple of cleaning processes is discussed later in the section. Two different capping agents have used to stabilize ZnO nanoparticles. UV-Vis Spectroscopy and scanning electron microscopy have been used extensively to characterize the samples. The experimental details are as follows-

### **2.1-Preparation of ZnO nanoparticles by Zinc acetate and sodium hydroxide with PVP(polyvinyl pyrrolidone) as capping agent in isopropanol ( Sample A):**

In our very first experiment we prepared ZnO nanoparticles in isopropanol solution and capped that with PVP. Zinc acetate ( $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ , from Aldrich, 0.01 mmol) was dissolved in 1.6 ml of 2-propanol under vigorous stirring at 50 °C. The solution was diluted to a total volume of 20ml followed by chilling to 0 °C. PVP was added into the above flasks under vigorous stirring to prepare solution having 5:3 molar ratio of Zinc acetate to PVP. The mixture was then hydrolyzed in an ultrasonic bath at room temperature by the following procedures: 1 mL of a  $2 \times 10^{-2}$  mol/L NaOH solution (GR grade) in 2-propanol (HPLC grade) was added drop wise to each of the above four diluted and cooled precursor solutions using a separation funnel, and the reaction was maintained for ~2h. Finally ZnO nanoparticle solution was analyzed by taking UV-Vis spectra and SEM images of the sample which are discussed in the results and discussion section.

## **2.2-Preparation of ZnO nanoparticles in n-propanol by using Zinc acetate and Sodium Hydroxide:**

A simple method for preparation of ZnO nanoparticles without using any capping agent is given in [3] in which due to excess amount of Zinc acetate taken, solution remained stable upto 2 months. We used this method for preparation of ZnO nano colloidal solution. 27.5mg of Zinc acetate di-hydrate was added to 10 ml of Propanol -1 and vigorously stirred at 50<sup>0</sup>C for few minutes. In another solution 8mg of Sodium Hydroxide was added to 10 ml of Propanol and vigorously heated at 60<sup>0</sup>C for few minutes. 4ml of zinc acetate solution was taken and diluted to 36 ml with additional Propanol-1 and 4 ml of NaOH solution was diluted to 14 ml. These two solutions were mixed and heated at 55<sup>0</sup>C and allowed to react in a water bath for 16 min with vigorous stirring. After completion of reaction solution was cooled to the room temperature and then UV-Vis spectra was taken with the help of Double beam spectrophotometer.

Same reaction with double the concentration (**Sample B**) was done and results obtained were found to be very much same with increased particle concentration so this double concentrated solution was used for further experimentation. As Sodium acetate formed during the reaction and excess of Zinc acetate taken were also present in the solution which might alter the properties of the film so we tried to purify the solution using two different capping agents to cap nanoparticles and various washing procedures remove impurities.

## **2.3-Capping Of ZnO nanoparticles with DDT**

To remove the impurities from the initially prepared solution we needed to wash the solution. Washing could be done with the help of ethanol and water to make solution washable we capped the particles with DDT(Dodecanethiol)( **Sample B**). In 50 ml of solution 10 $\mu$ l DDT was added but immediately after the addition solution became translucent, solution was left overnight for capping in a refrigerator UV-Vis Spectra for DDT capped Particles was also taken next day.

## **2.4-Capping of ZnO nanoparticles of Experiment 2 with PVP**



Before preparation of nanoparticles by method discussed above 25 mg of PVP in 5 ml propanol was added and a transparent solution containing ZnO as suggested by UV-Vis spectra was obtained (Sample C).

## **2.5-Washing of sample B**

### *Washing with ethanol and acetone only*

To remove the excess amount of Zinc acetate, Sodium Acetate and DDT present in the Sample B It was washed with the help of ethanol and acetone. First by centrifuging at 2000 rpm for 15 min particles were settled down, a white colour precipitate was found at the bottom of centrifuge which was dispersed in ethanol, sonicated for 5 min and precipitated again using centrifuge. It was re-dispersed in acetone and re-precipitated. Finally the white colour precipitate was dispersed in Chloroform and a transparent solution was obtained which showed the presence of ZnO nanoparticles in UV-Vis data but amount of absorption reduced significantly as discussed in results and discussion section. SEM images of the sample were taken and discussed in results and discussion section.

### *Washing with Ethanol , Water*

As discussed in Results and discussion section results obtained after ethanol and acetone washing had shown presence of some impurities in SEM images so we Introduced another step of water washing instead of acetone washing. So precipitate obtained after the ethanol wash was washed with 8ml of water but during the water washing DDT was phase separating and particle loss increased up to a very high level almost no precipitate was obtained and all the DDT capped particles were accumulated either on the walls of the tube or formed the layer over the water. To collect these particles 1ml of Chloroform was added from the walls and center of the tube and after shaking left for 5 min to allow separation of two liquids. Chloroform settled at the bottom and layer of water above it was carefully removed with the help of a glass dropper UV-Vis Spectra and SEM images for this sample were taken and discussed in results And discussion Section.

### Two times Ethanol washing

As satisfactory results could not be obtained from the above two methods so instead of washing with water we washed the Sample B two times with ethanol and precipitate was then dispersed in Chloroform results for which is discussed in next section.

### **2.6 Fabrication of array by Evaporation guided self assembly System**

A silicone wafer was cleaned with aqua-regia, acetone and chloroform and then Ozonized for 10 min. immediately after the ozonization 10 $\mu$ l of ZnO nanocolloidal solution dispersed in toluene were dropped on the wafer.

### **3.Results and discussion:**

UV- Vis spectra of various samples was taken which to confirm the presence of ZnO nanoparticles. With the help of UV-Vis spectra particle size is calculated and compared with the help of SEM images obtained. Equation Used for the size calculation is obtained from literature as-

$$0.181d^2 + 0.414d + 0.008 = 1/\Delta E_g \quad (\text{eq-1})$$

Where  $\Delta E_g$  is Difference of  $1239/\lambda$  ( absorption onset wave length) and actual band-width of bulk ZnO. For absorption onset of 360 nm calculated particle size is around 5nm.

Sample wise results obtained are as follows:

#### **3.1-Results and discussion for Sample A**

UV-Vis spectra obtained immediately after the completion of reaction for sample A is shown in fig-3 which shows a shoulder around 330 nm SEM images also did not show

particles present in the sample may be because Zinc acetate concentration taken was too low compared to PVP concentration and layer of organic had covered the particles.

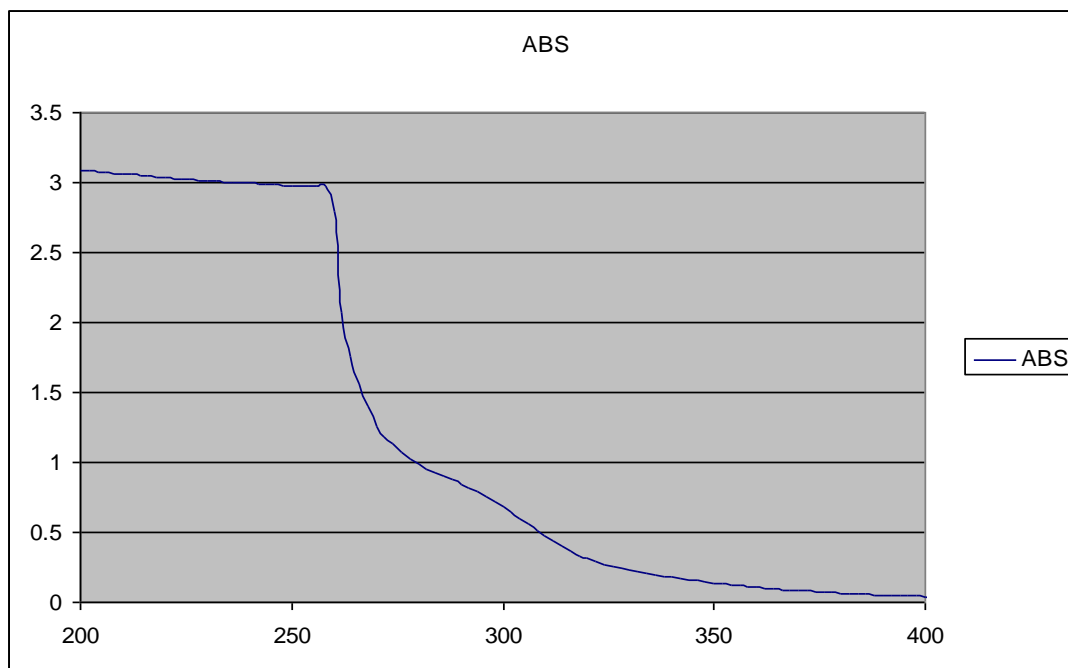


Fig-3 (Immediately after the reaction Sample A)

### **3.2-Results for Sample B:**

Extensive amount of experimentation has been done on sample B to obtain particles and then to remove impurities. Fig-4 shows the UV-Vis spectra of sample B immediately after the reaction. It shows absorption onset around 360 nm which according to eq-1 correspond to around ~5nm particles. SEM image for this sample was taken and shown in Fig-5. SEM images show the presence of around 5nm particles. Then these particles were capped with DDT and as 10 $\mu$ l of DDT was added sample became translucent due to base line absorption as suggested by Eva M. Wong et. al.[5]. UV –Vis spectra for the sample after DDT capping is given in Fig-6 which does not show clear picture due to interference by DDT but later after precipitating and dispersing in chloroform ZnO hump around 360 is quite clear. This translucent solution was centrifuged at 3000 rpm for 20 min to precipitate all the particles and then washed with first ethanol and chloroform but that didn't give good results as observed by the SEM images for the sample. Then we

washed the sample first with ethanol and then with water. UV-Vis spectra and for supernatant and dispersion is taken after each step and is shown in figures below.

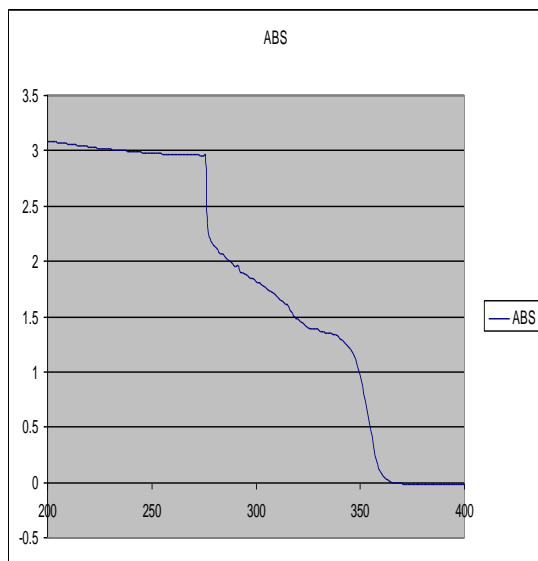


Fig-4 (immediately after the reaction Sample B)

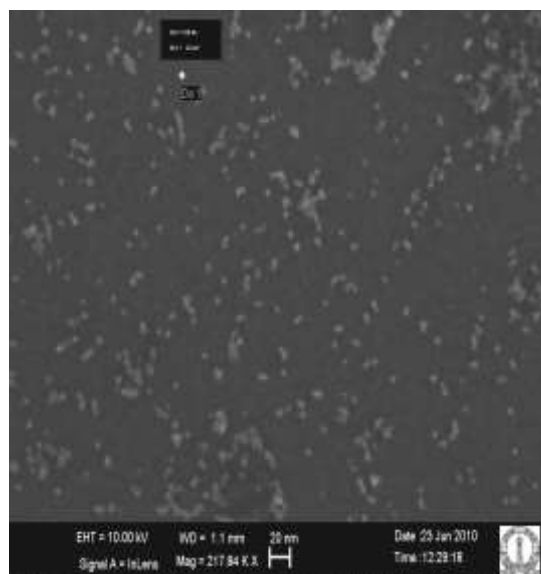


Fig-5 (immediately after the reaction Sample B)

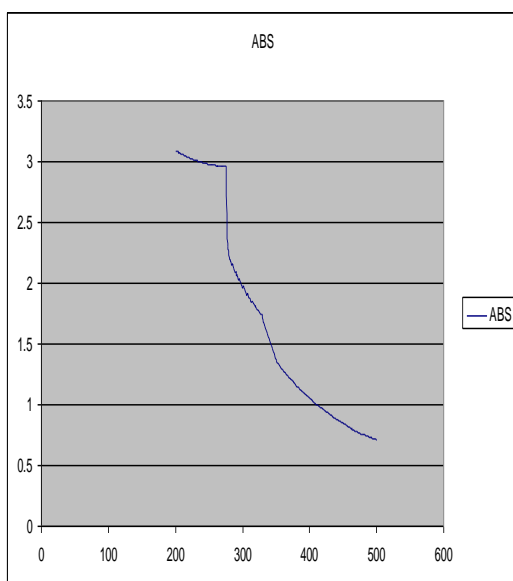


Fig-6( DDT capped ZnO particles)

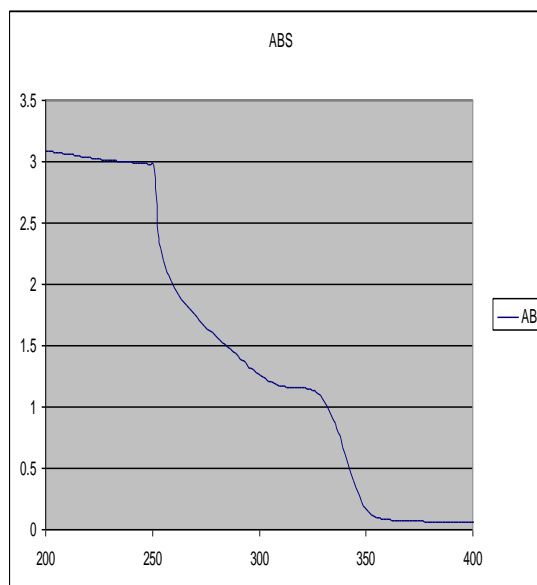


Fig-7( after precipitation from propnol dispersion in Chloroform)

. Supernatants do not show any ZnO hump so particle loss should not be significant.

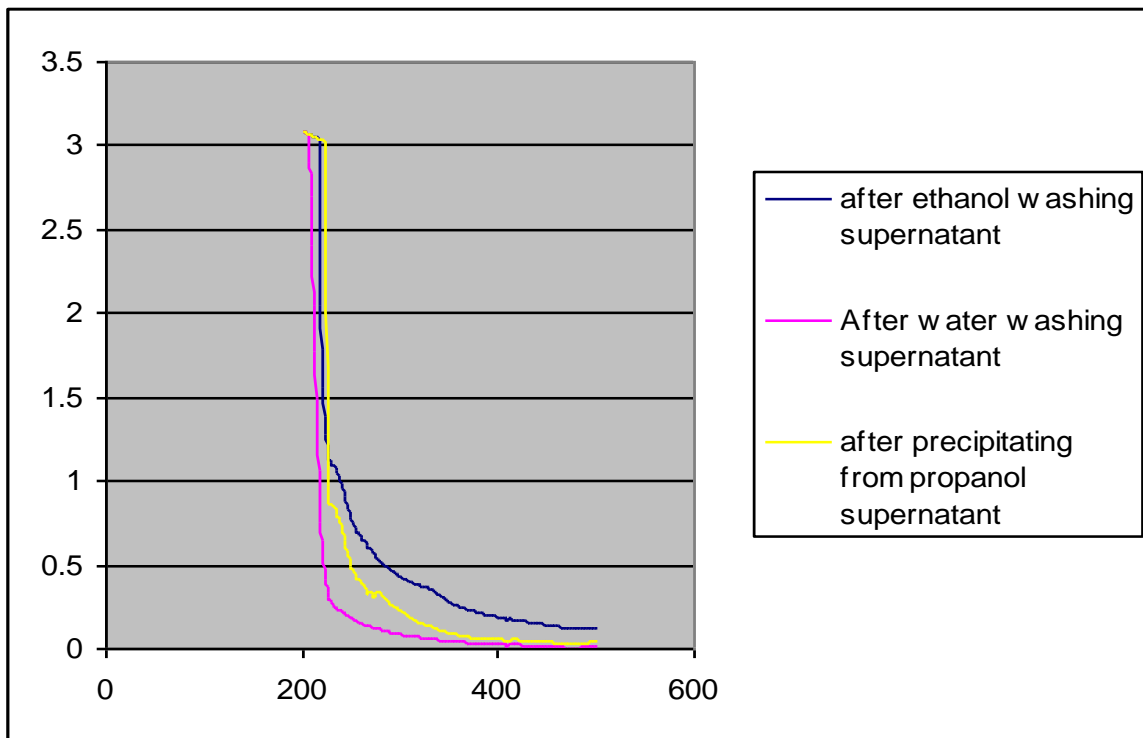


Fig-8(UV-Vis of Supernatants)

To analyze the degree of interference of precursors with UV-Vis spectra UV-Vis spectra for Zinc acetate, Sodium acetate and DDT was also taken and shown in fig- 9.

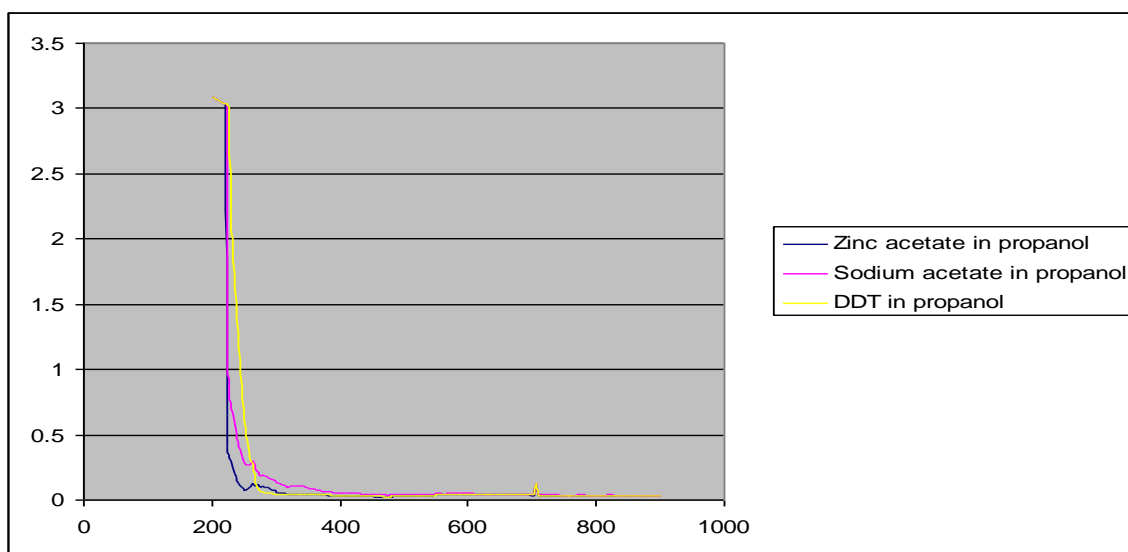


Fig-9( UV-Vis for precursors)

After washing from water DDT capped particles were phase separating so all the particles formed a layer over the water surface or stacked to the wall of centrifuge tube. To collect

these particles 2ml of chloroform were added as described in experiment section and UV-Vis spectra for the final particles dispersed in chloroform is given in fig-10. It shows the presence ZnO nanoparticles as observed by absorption onset around 360nm.

4 $\mu$ l of this sample were taken for SEM and image obtained is shown in Fig-11

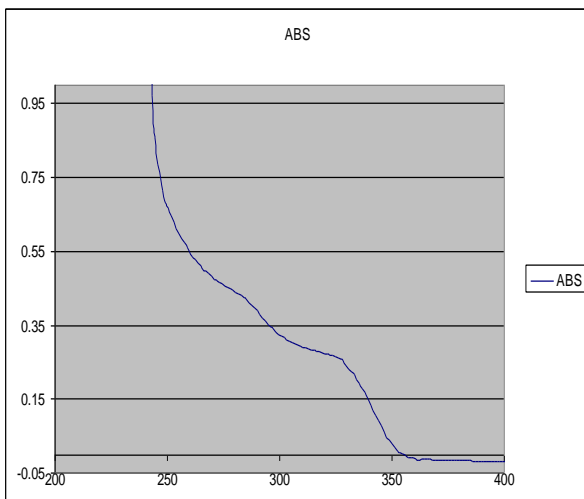


Fig-10 after ethanol and water washing particles dispersed in chloroform)

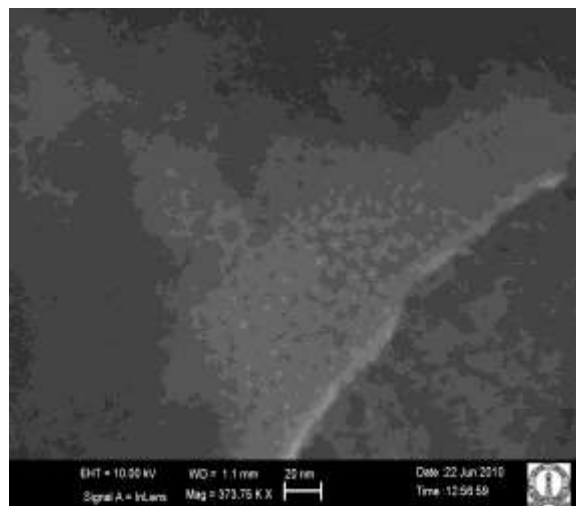
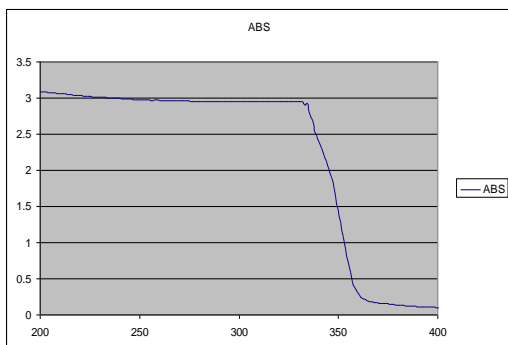
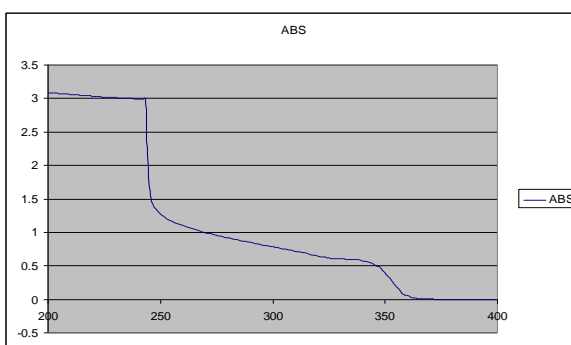


Fig-11( after ethanol and water wash particles)

SEM images show presence of a layer over the particles which might be some impurity. Because Phase separation of DDT capped ZnO in water was creating problem earlier so instead of washing with water we washed the sample twice with ethanol. After two times ethanol washing particles from one centrifuge tube were dispersed in Chloroform and for other tube were dispersed in toluene. UV-vis spectra and SEM image of particles dispersed in chloroform is given in fig-12 and 13.



(1)



(2)

Fig-12- After washing of 15 ml of original solution particles dispersed in (1) 3ml of Chloroform (2) diluted further to 30 ml.

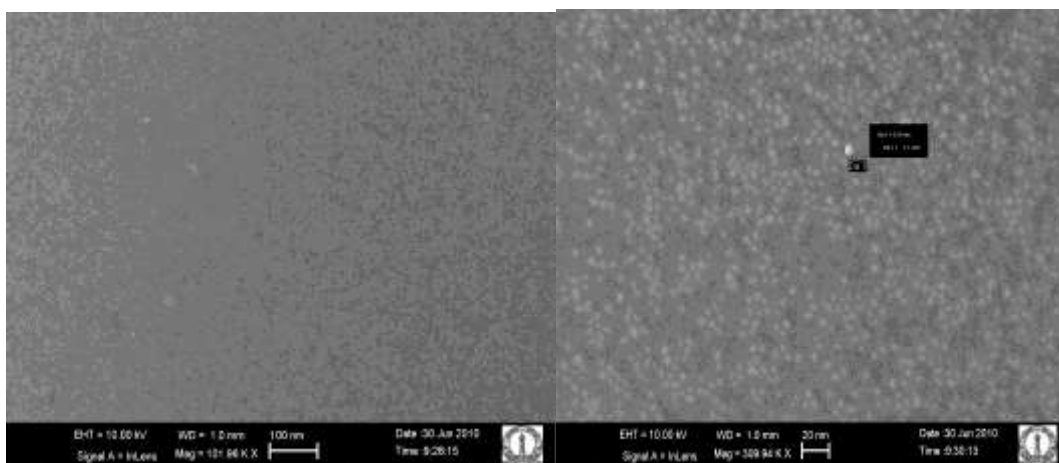


Fig-13 SEM images of Fig 12 (2)

Another colloidal solution in toluene was used for fabrication of array by evaporation guided self assembly method SEM image obtained for the sample is shown in fig 14-

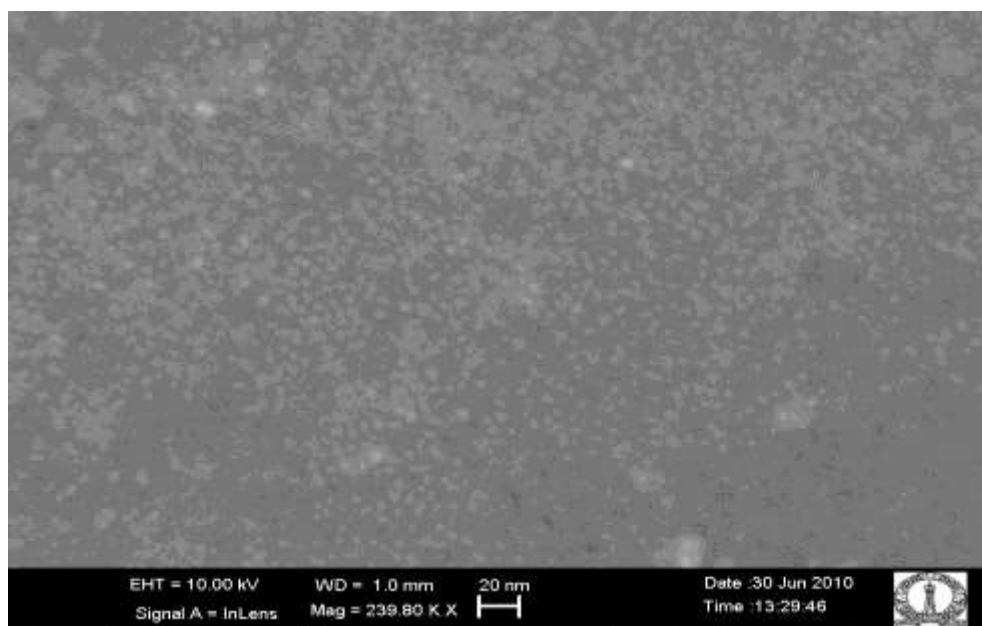


Fig-14 ( array formed by evaporation guided self assembly method) though particles are arranging but still sum patches are also present in SEM image. Another SEM image for the particles dispersed in chloroform (Fig-12(2)) was also taken after 1min ozonization of the sample and it shows( fig 15) that particles are fusing

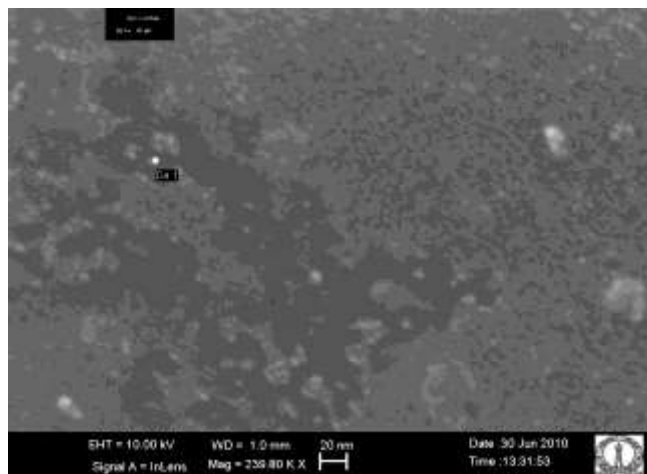


Fig-15 SEM image after 1 min ozonization of Fig-12(2) sample

### **3.3-Results and Discussion for Sample C**

Another sample (Sample C) was prepared using PVP as capping agent. UV-Vis spectra for the sample are shown in fig-16

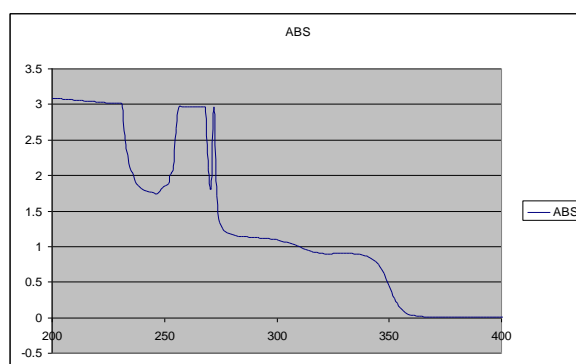


Fig-16( Immediately after the reaction)

In SEM images of the sample formation of nanotube kind of structure was also observed with particles as shown by fig-17 and 18

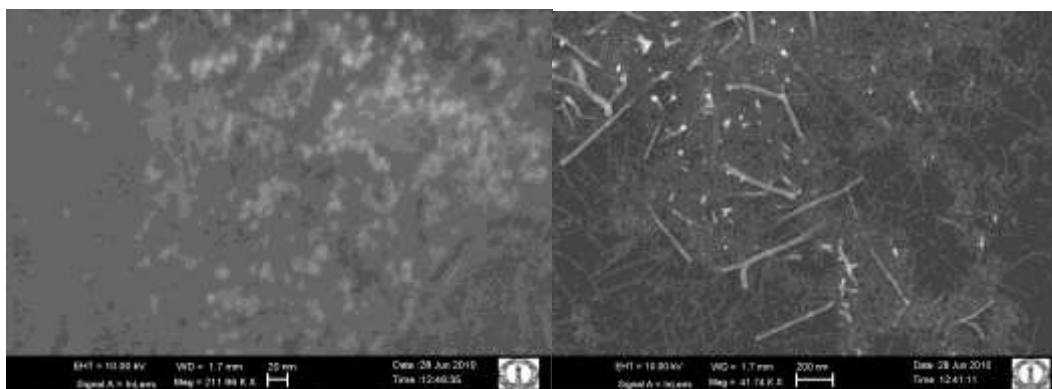


Fig-17 ( formation of nanotubes with particles)





Fig-18 ( PVP capped ZnO nanoparticles)

#### **4. Conclusion and Future Work:**

ZnO nano-colloidal solutions were prepared by three different methods as discussed above. One sample (sample B) was capped with Dodecane thiol and was extensively experimented for washing and array fabrication. Washing was done with various methods in which best results were obtained by two times ethanol wash at 3000rpm for 20 min. After washing particles an array of particles was fabricated by evaporation guided self assembly method.

Other sample ( Sample C) was capped with PVP which show formation of nonotube kind of structure with Particles.

As array formed by self assembly method does not show a clear hcp structure of spherical ZnO np's and concentration of solution is good enough to be used for the spin coating or assembly by controlling the curvature of water. After fabrication of film uniformity, conductivity and transparency of film can also be measured in future.

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