

# **Chapter 7**

## **Overall Conclusions**

## CHAPTER 6

### Overall Conclusions

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The suspensions of light absorbing and conducting nanomaterials (nanofluids) have been successfully utilized for efficient absorption of solar thermal energy in conventional heat transfer fluids such as water, ethylene glycol and silicone oil. Furthermore, efficient solar desalination of hard water and sea water has been effectively demonstrated with the help of nanofluid based approach. The efficiency of solar thermal heating of water, ethylene glycol and silicone oil and solar desalination has enhanced significantly by using various nanomaterials such as copper (Cu), aluminium (Al), copper oxide (CuO), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), zinc oxide (ZnO), titanium dioxide (TiO<sub>2</sub>) and carbon. It has been found that particle concentration in base fluid along with size and shape of nanomaterial has profound effect on efficiency of the process. Apart from this, it was observed that doping with small amount of noble material such as silver (Ag) or the material exhibiting strong photothermal effect such as carbon also helps to extend the range of solar energy absorption of the nanomaterial.

Efficiency of solar energy absorption is the important parameter and it gives the percentage of absorbed radiation to the incident radiation. The nanoparticle concentration in base fluid has been found to affect the efficiency of solar energy absorption significantly. Lower particle volume fraction concentrations (0.025 and 0.05%) have shown better efficiency values in case of most of the nanomaterials (Al, CuO, Fe<sub>2</sub>O<sub>3</sub>, ZnO QDs, ZnO NWs, TiO<sub>2</sub> P90, TiO<sub>2</sub> NWs, Carbon). Efficiency was found to decline due to sedimentation of particles occurring at higher particle concentrations. Since nanosized particles have large surface energy, high particle concentration led to the agglomeration effect, causing particles to come together and form bigger size particles. Since large size particles settle down more rapidly, therefore higher particle concentrations are not recommended in the nanofluid solutions. Higher particle concentrations also have shown increased efficiency at few instances (in case of Cu, 23 nm SiO<sub>2</sub>, TiO<sub>2</sub> P25, TiO<sub>2</sub> NTs). This was because, either suspensions were stable or there was marginal increase in the efficiency observed with increase in particle concentration, which is not appealing from economic point of view. In addition to the particle concentration, varying the particle size can also be used to enhance the efficiency. It has been observed that as particle size increases efficiency was found to

decrease (for SiO<sub>2</sub> nanoparticles of size 23, 65 and 325 nm and carbon nanoparticles of size 30, 65 and 325 nm). This is ascribed to the fact that, effective surface to volume ratio available for photothermal absorption decreases with increase in the size of nanoparticles. Also stability of nanofluid was found to decrease with increase in the size of the nanoparticle. Non-uniform, unstable suspensions with lower surface area to volume ratio led to the decline in the efficiency. The effect of shape of the nanoparticles also was studied and it was found that quantum dot are more appealing than nanowires in case of ZnO whereas TiO<sub>2</sub> NTs were found to be best than other TiO<sub>2</sub> nanostructures (spherical particles and nanowires). Furthermore, Ag doping of SiO<sub>2</sub> (23 nm) and carbon doping of TiO<sub>2</sub> (P25) revealed significant improvement in the efficiency compared to only SiO<sub>2</sub> and TiO<sub>2</sub>.

Several nanomaterials were synthesized in this study (Cu, CuO, SiO<sub>2</sub>, Ag-doped SiO<sub>2</sub>, ZnO QDs & NWs, C-doped TiO<sub>2</sub>, TiO<sub>2</sub> NTs & NWs, and carbon) other nanoparticles (Al, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> P25, TiO<sub>2</sub> P90, carbon-30 nm) were obtained commercially. Studies on synthesis of Cu nanoparticles revealed that, as amount of reducing agent was increased from 10 gm to 20 gm, particle size was found to decrease by 50 %. SLS (anionic) and myristic acid (non-ionic) gave pure crystalline copper without impurities compared to PVP (amphiphilic) and CTAB (cationic). Studies on concentration of surfactant shows that, increase in concentration of surfactant decreases the size of the particles. Use of SLS gives small and uniform particle size distribution. PVP gives well separated, perfectly spherical particles with narrow size and shape distribution. Considering all important parameters such as purity, size and shape distribution, anionic surfactant (SLS) was better choice over the other types. Copper oxide nanomaterial was synthesized with variation of different reaction parameters such as effect of amount of base (NaOH), initial concentration of starting reagents and surfactant on the size, shape and morphology of final product. It has been observed that as concentration of NaOH was increased from 0.25M to 0.5M, crystal size was found to decrease by 40%. SEM results show the sheet like morphology of synthesized CuO nanomaterial. The nanopowder loses its sheet like morphology at higher concentrations of NaOH (for 0.5M and above). This could be attributed to the fact that as base concentration was increased, greater number of initial nuclei were formed leading to formation of smaller size particles. It was evident that size of CuO nanomaterial decreases with increase in dilution. Decrease in the size of nanomaterial with dilution was attributed to the fact that initial nuclei formed have no further supply of the new

nuclei for their growth once the precursors were exhausted due to low concentration of starting reagents. It is evident from the SEM analysis that as amount of PVP increased from 0.5 g to 1.5 g, shape of the material changes from fibrous sheets to particulate agglomerate.

Monodisperse spherical silica nanoparticles (325 nm) were synthesized by well-known Stober's method. FESEM images of SiO<sub>2</sub> nanoparticles clearly showed monodisperse spherical size silica nanoparticles with average size of 325 nm. Since Stober's method usually gives large size particles, novel microwave assisted method for synthesis of SiO<sub>2</sub> nanoparticles was developed. Use of microwave irradiation was found to considerably reduce the reaction times by one twelfth. The analysis showed the small size particles with size range between 40 and 91 nm with average particle size at 65 nm. Two times dilution of starting reagent in same method reduced the SiO<sub>2</sub> nanoparticles size to 23 nm almost by one third. Ag-doped silica nanoparticles (23 nm) were synthesized by using reported method. ZnO QDs were prepared by using reported method in aqueous solution instead of alcoholic solution. Reaction was carried out under high pressure of 6 bar under constant stirring at 50 rpm instead of autogenous pressure reported in hydrothermal synthesis. FESEM analysis reported wire diameter in the range of 200 to 300 nm. Nanowires obtained were hexagonal cross section with uniform size and shape. TiO<sub>2</sub> nanotubes and nanowires were synthesized in the laboratory by using ultrasound assisted hydrothermal method by using reported method with the reactor pressure being an additional parameter. FESEM analysis showed nanotube diameter in the range of 12 to 29 nm and nanowire diameter in the range of 15 to 29 nm. Further, carbon doped TiO<sub>2</sub> were synthesized by using hydrothermal method with reactor pressure being the additional parameter. FESEM analysis depicted size of the C-doped TiO<sub>2</sub> nanoparticles in the range of 20 to 40 nm. Carbon nanoparticles were synthesized by using hydrothermal method. The reaction was carried out in high pressure reactor under controlled mixing, temperature and at pressure conditions as opposed to hydrothermal bomb reported in the literature wherein these controls are not possible and reactor operates under autogenous pressure conditions. For same reaction time reported in the literature, high pressure reactor based approach gives, one fifth of the size for 12 h and one third size for 3 h reaction time for carbon nanoparticles. Therefore, it can be concluded that, controlled conditions of temperature, high pressure and uniform mixing reagents yield lower particle sizes than

reported in the literature for similar conditions with hydrothermal bomb reactor having no control over these conditions.

These nanoparticles were dispersed in water, ethylene glycol and silicone oil in four different particle volume fraction concentrations (0.025, 0.05, 0.1 and 0.3%). Efficiency of solar energy absorption was determined for every nanofluid solution. Studies using water as a base fluid revealed that, Cu nanoparticles (100 nm) showed promising results at 0.3% particle concentration (by volume) with remarkable enhancement in the efficiency of about six times compared to the value of water without nanoparticles followed by 30 nm carbon (nearly 4 times), 133 nm CuO (3 times), Fe<sub>2</sub>O<sub>3</sub> (2.3 times), Al (2.2 times) and TiO<sub>2</sub> NTs (2 times). For CuO, it was observed that decrease in the size of nanomaterial from 133 to 108 nm increase efficiency by 7%. However use of PVP as a surfactant to reduce the size of CuO nanomaterial to 90 nm could not help to improve the efficiency despite of lower size of CuO due to the thermal barrier layer developed by surfactant on the surface of particles. SiO<sub>2</sub> (23 nm) showed much appreciable efficiency enhancement of 91%. As SiO<sub>2</sub> nanoparticle size was increased from 23 to 325 nm, efficiency value was declined significantly and there was only 23% enhancement observed at 325 nm size SiO<sub>2</sub> particles. One dimensional nanostructure of TiO<sub>2</sub>, especially TiO<sub>2</sub> NTs have shown appealing results in the semiconducting materials category. Carbon doping of 21 nm TiO<sub>2</sub> improved efficiency by more than 12%. Reduction in the particle size of carbon also found to produce detrimental effects. The efficiency was found to decrease with increase in the carbon nanoparticles size from 30 to 325 nm.

Experiments were also conducted with ethylene glycol (EG or MEG) as a base fluid. Carbon nanoparticles have proved to be the best material possible for this base fluid among the studied materials. Efficiency enhancement of about two times was observed in case of carbon (30 nm). However, increase in the size of the particles led to decrease in the efficiency. Though, carbon (325) showed 50% enhancement in the efficiency. The other promising materials reported for MEG as a base fluid also showed considerable enhancement in the efficiency with TiO<sub>2</sub> P90 (14 nm) being 54%, C-doped TiO<sub>2</sub> (50%), Fe<sub>2</sub>O<sub>3</sub> (45%), 133 nm CuO (42%), etc. Silicone oil was also investigated for possible improved solar energy absorption after addition of nanoparticles. For silicone oil again carbon was found to be best material with highest efficiency enhancement of about 2.6 times at 30 nm size, followed by CuO (96%), Cu (82%), Fe<sub>2</sub>O<sub>3</sub> (70%), ZnO QDs (70%) and C-doped 21 nm TiO<sub>2</sub> (56%), etc. Therefore, it can

be concluded that, significant enhancement in the solar energy absorption can be achieved with the help of above mentioned nanomaterials.

Solar desalination experiments with various nanomaterials reported that, iron oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticle have shown notable decrease in desalination time (3 times) for getting fixed amount of desalinated water. Efficiency was found to increase with increase in concentrations of Cu, Al,  $\text{Fe}_2\text{O}_3$ , ZnO and carbon. However, for CuO,  $\text{TiO}_2$  P25/P90/Nanotubes/Nanowire, silica higher efficiency was reported at low concentrations.  $\text{Fe}_2\text{O}_3$  nanoparticle showed about 3 times enhancement in the solar desalination efficiency compared to the value of hard water without nanoparticles followed by 30 nm carbon (2.5 times), 133 nm CuO (2 times),  $\text{TiO}_2$  NTs (96%), Cu (90%), Ag-doped  $\text{SiO}_2$  (72%), Al (68%),  $\text{TiO}_2$  NWs (60%), etc. Few selected promising materials were also studied for solar desalination of sea water (artificially prepared as per ASTM standards). It has been found that Cu nanoparticle show maximum enhancement of 2.9 times in the solar desalination efficiency followed by carbon (2.4 times),  $\text{Fe}_2\text{O}_3$  (2.2 times), CuO (1.7 times), Al (80%),  $\text{TiO}_2$  NWs (46%) and  $\text{TiO}_2$  NTs (45%), etc. Therefore, it can be concluded that solar desalination times can be significantly reduced by enhancing the efficiency of overall process with the help of above listed promising materials.

However, suspending light absorbing and conducting nanoparticles such as Cu, CuO,  $\text{TiO}_2$  (P25: 21 nm),  $\text{SiO}_2$  (65 nm) and carbon nanoparticles into azeotropic mixtures such as ethanol-water and isopropanol-water and subsequent solar distillation experiments did not yield any significant results in the form of separation of mixture at azeotropic composition. Distillate composition was found to be the same as that of initial composition (azeotropic composition). Therefore, it has been concluded that this method does not lead to separation of ethanol-water and isopropyl alcohol azeotrope.

Overall, it can be concluded that light absorbing, conducting nanomaterials are promising materials for solar energy absorption in water, ethylene glycol and silicon oil and for solar water desalination.